EXERCISES IN CHEMICAL CALCULATION

BY

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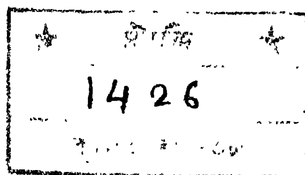
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PREFACE

In common with many other teachers of chemistry, the compilers of this volume believe that the working of suitable numerical examples is the best aid to the understanding of the quantitative aspect of chemical phenomena. The ideal calculations are those made by the student from his own experimental data, but it is necessary for him to use the figures of other workers and the data of experiments which he himself cannot perform. For this reason the following set of numerical examples has been compiled. It is drawn from recent examination papers and from various original sources. A number of the examples available in examination papers have been rejected because they had no conceivable relation to possible experimental conditions, and were therefore misleading.

In most of the chapters a concise explanatory statement precedes the questions for solution. It is not intended that this should take the place of wider reading and study, but rather that it should indicate the portions of the text-book relevant to the particular subject under discussion, and provide a brief summary of what should be found there. It is believed, however, that the matter is put in its correct order, that it is in accord with present-day knowledge, and that certain of the beginner's difficulties are explained more clearly than is often the case. Dogmatic rules for obtaining an answer have, it is hoped been avoided.

Nowadays the teacher of chemistry finds it unnecessary, as a rule, to give preliminary lectures on elementary physics. At the same time, it is noteworthy that most students learn the application of Boyle's law and of Charles' law from their chemical training. Hence this book deals less with elementary physics than has been the case in previous works of the same character, but contains some simple exercises on the two laws mentioned. It is assumed that the student has a working knowledge of the metric system, and it is desirable that he should understand the use of logarithms. It is also considered advisable to insist from the outset that careful attention be paid to the significance of the digits in experimental numbers and in results calculated from them, a subject which receives too little attention even in some original papers in the chemical and physical journals. Only in this way is it possible to avoid confusion in such a case as the choice between an approximate and an exact atomic weight for a particular purpose. In adhering to this principle, it has been necessary to make slight alterations in certain of the examples obtained from examination papers and other sources, *e.g.* the substitution of "1·000 gram" or "1·0000 gram," as the case may seem to demand, for the expression "one gram." Where any change in the statement of a copied question has been introduced, the word "adapted" is added. This is done in order to avoid omission of several slightly faulty questions which, with some alteration, become valuable.

As regards the standard of difficulty, most of the chapters contain some questions suitable for beginners, and others for advanced students. The beginner should find little difficulty in choosing suitable ones for himself from the neighbourhood of those taken from Intermediate Science examination papers.

The thanks of the compilers are due to the authorities of the Universities of Manchester, Leeds, and London, of the Institute of Chemistry, and to the Controller of H.M. Stationery Office, for permission to reprint calculations from the examination papers under their control. Their thanks are also due to the Controller of H.M. Stationery Office, and to Messrs. Macmillan & Co., Ltd. for permission to reproduce the four-figure logarithm table at the end of the book; and, finally, to Mr. F. W. Atack, B.Sc. Tech., for checking many of the answers.

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May, 1912.

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EXERCISES IN
CHEMICAL CALCULATION

CHAPTER I

INTRODUCTORY—CALCULATIONS FROM EXPERIMENTAL DATA

ONE of the principal difficulties which confront the student in making numerical calculations from experimental data is that of deciding the number of figures he shall retain in his final result. If, for instance, the fraction $\frac{11}{7}$ is to be expressed in decimals, the ordinary arithmetical process may be carried out until the figure $1{\cdot}\dot{5}7142\dot{8}$ is obtained. As the quotient in dividing exactly 11 by exactly 7, this is a perfectly correct solution. But in scientific measurements there is no such thing as exactly 11, because every measurement is subject to a certain error of observation. It is advantageous for such measurements to be expressed in figures which show not only the numerical result obtained, but also the accuracy with which the measurement has been made. When the weight of a crucible is said to be 11 grams it is usual to assume that the weight is known to the nearest gram, *i.e.* it is more than 10·5 and less than 11·5. Similarly, if the weight is given as 11·0 grams it is known to be more than 10 95 and less than 11·05, and so on. In this way it is recognized that the number 3·8342 is subject to a possible error of ± 0·00005 or about 1 part in 80,000.

If this be borne in mind it will be quite clear that in calculations from such numbers all the possible errors

in the data will be transferred to the result of the calculation. Consequently the result will be subject to at least the same uncertainty as the least accurate of the data, and the final figure must be made to express that fact. It is therefore obvious that in adding together

$$\begin{array}{r} 10{\cdot}7251 \\ 1{\cdot}9 \\ 2{\cdot}35 \\ \hline 14{\cdot}9751 \end{array}$$

the last three figures of the sum have no significance, for the number 1·9 has a possible error of ± 0·05, and the sum may have at least this error. The result will therefore be correctly expressed by 15·0, though if the number is to be used in further calculation it is advisable to retain one more figure and write 14·98. (In choosing the above figures a process of rounding off has been used in which it will be seen that the last figure retained has been increased by unity because the portion discarded was equal to more than half such a unit. If the sum had been 14·9215, the figures would have been 14·9 and 14·92 respectively.)

The above arguments may now be illustrated by further examples—

$$760 - 12{\cdot}7 = 747$$
$$0{\cdot}031 \div 17{\cdot}624 = 0{\cdot}0018$$
$$441{\cdot}46 \div 0{\cdot}921 = 479$$
$$0{\cdot}012786 \times 12{\cdot}2 = 0{\cdot}156$$

In the first case the result cannot be given as 747·3 because the original 760 is presumably only correct to the nearest unit. In the other cases the calculation is only carried so far as to produce a figure in which the accuracy is of the same order as in the least accurate of the data.

It will further be seen that recurring decimals have

no practical significance since they represent quantities in which the figures after the decimal point may be continued indefinitely, *i.e.* in which the possible error is infinitely small.

A difficulty which may sometimes arise is illustrated in multiplying 1728 by 1·2. The product, 2073·6 obviously contains three meaningless figures. It would not be much more satisfactory to express the result as 2100, *i.e.* 2100 ± 0·5. A convenient method in such cases is to express the above result, for instance, as $2·1 \times 10^3$.

It will be clear from the results obtained above that it is not necessary to carry out the whole arithmetical process with all the figures available, since the same solution can be obtained by dispensing with unnecessary digits in the more accurate numbers, *e.g.* in 0·031 ÷ 17·624, it is quite sufficient to use 0·031 ÷ 17·6. Therefore, as a general rule, when a number of figures are to be subjected to multiplication or division it is advisable to—

(I.) Inspect the numbers given, and decide which one shows the smallest degree of accuracy.

(II.) Round off all the other numbers so that they contain at most only one more significant figure than the least accurate number. For example—

$$\frac{0·0060 \times 760·0 \times 292·43}{33·023 \times 763·3 \times 273·0 \times 0·0000899}$$

In this case the number 0·0060 is much less accurate than any of the others, and since this contains two significant figures the others may be rounded off to contain three, while the final result will only be correct to one part in 120. The expression is simplified to—

$$\frac{0·0060 \times 760 \times 292}{33·0 \times 763 \times 273 \times 0·0000899}$$

the result being 2·15. This figure, however, is subject to an error greater than 0·005, which is, in fact, nearly 0·02. So the result might be given as 2·15 ± 0·02.

When the numbers for calculation have been suitably rounded off, the calculation itself should be carried out by abbreviated methods of multiplication and division, or better still by the use of logarithms. In the latter case it is necessary to use logarithm tables calculated to a suitable number of figures. Four-figure tables will suffice for most chemical calculations, although in special cases five-figure or even seven-figure tables may be necessary.

The above arguments are all concerned with the accuracy of observations, *e.g.* the accuracy of a weighing, of the reading of a volume from the scale on a burette, or of a thermometer reading. This is quite distinct from error in the experimental processes connected with the observation. If, for instance, the amount of sodium chloride in a solution has been estimated by evaporating the water, the errors of observation (weighing) may have been only, say, 0·02 per cent.; the result is correctly calculated when carried out to this degree of accuracy (0·02 per cent.). The actual process, which is supposed to be the complete separation of water from sodium chloride, may have been imperfectly carried out, *i.e.* some water may have been retained in the residue, or some sodium chloride may have been lost. It would be mere coincidence that the errors due to these two causes should balance each other, so that the process is subject to experimental errors which are quite distinct from the errors due to lack of sensitiveness of the measuring instrument (the balance).

What concerns us in the following pages is that the result, without containing any superfluous figures, shall be expressed as accurately as the data permit.

CHAPTER II

THE LAWS OF CHEMICAL COMBINATION BY WEIGHT —CHEMICAL EQUIVALENTS

To understand the laws of chemical combination it is necessary to be able to deduce them from experimental data. Since it is on these laws that the whole quantitative study of chemistry depends, it is not surprising that their exactness has been made the subject of searching investigation.

Law of the Conservation of Mass.—1·000 gram of oxygen will unite with 0·126 gram of hydrogen to form water weighing 1·000 + 0·126 = 1·126 gram. Many such experiments have been performed with various substances, with the highest degree of accuracy possible to modern science. The result is the establishment of the Law of the Conservation of Mass, which states that **in any chemical or physical change, the total mass of the system remains constant.** (The mass of a body is measured by its weight.)

Law of Fixed Ratios.—This law deals with the relation between the masses of substances taking part in a chemical action. Berzelius in considering the formation of lead sulphide from its elements found that—

(I.) 25·000 grams of lead produced 28·855 grams of lead sulphide.

(II.) 15·000 grams of lead produced 17·3125 grams of lead sulphide, *i.e.* one gram of lead produced—

$$\left.\begin{array}{ll}(\text{I.}) & \dfrac{28{\cdot}855}{25{\cdot}000} = 1{\cdot}1542 \\ (\text{II.}) & \dfrac{17{\cdot}3125}{15{\cdot}000} = 1{\cdot}1542\end{array}\right\} \text{gram of lead sulphide.}$$

Thus the combining quantities of lead and sulphur are in the constant ratio of 1 : 0·1542. The same conclusion is reached when other reactions are considered, and the more carefully the experiments have been performed, the more concordant have been the results. The constancy of ratio is not confined to the combination of two elements to form a compound, but is always found between the weights of any number of substances (elements or compounds) reacting in the same way. The general expression of these facts is the **Law of Fixed Ratios**, which has been stated as follows:—

Definite chemical compounds always contain their constituents in fixed and definite proportions, or—

If several substances react together, then their masses as well as those of the new bodies formed always bear fixed proportions to each other.

Examples.—(If logarithms are used for the examples in this section, seven-figure tables are necessary.)

Show how the numbers of questions 1 and 2 illustrate the exactness of the law of definite proportions.

1. Berzelius synthesized silver sulphide. (Ostwald's *Klassiker*, 35, p. 89.)

2·605 grams silver gave		2·993 grams of sulphide		
10·00	„ „	11·49	„	„

Stas did the same with greater precautions. (*Brux. Acad. Sci. Bull.*, 1861, 255.)

59·4225	grams	of silver	gave	68·2482	grams	of sulphide
104·139	,,	,,	,,	119·6078	,,	,,
191·9094	,,	,,	,,	220·4158	,,	,,
150·000	,,	,,	,,	172·2765	,,	,,
249·076	,,	,,	,,	286·061	,,	,,

2. Stas (*loc. cit.* 1861, pp. 237–248) prepared silver chloride from metallic silver in a variety of different ways and obtained—

	Weight of silver.	Weight of silver chloride.
I.	91·462 grams	121·4993 grams
II.	69·8674 ,,	92·8145 ,,
III.	101·519 ,,	134·861 ,,
IV.	108·549 ,,	144·207 ,,
V.	399·651 ,,	530·920 ,,
VI.	99·9925 ,,	132·8382 ,,
VII.	98·3140 ,,	130·602 ,,

3. Calculate the percentage of oxygen in potassium chlorate from the following figures of Stas (*loc. cit.*, pp. 320, 321):—

	Weight of chlorate.	Weight of oxygen.
I.	69·8730 grams	27·3636 grams
II.	82·1260 ,,	32·1612 ,,
III.	86·5010 ,,	33·8705 ,,
IV.	132·9230 ,,	52·0430 ,,
V.	127·2125 ,,	49·8102 ,,
VI.	59·727 ,,	23·3830 ,,
VII.	95·7975 ,,	37·5020 ,,
VIII	147·318 ,,	57·6840 ,,

[*Note.*—The weight of the chlorate is correct to the nearest half milligram; Stas' results, given in the answers, are rounded off to correspond. The student may criticize Stas' last figure in the calculated percentage in one or two instances.]

4. Berzelius found that 10·000 grams of silver produced 13·275 grams of silver chloride; 30·000 grams of lead produced 43·900 grams of lead sulphate; 10·000 grams of lead chloride on treatment with silver nitrate formed 10·320 grams of silver chloride, which contained all the chlorine originally

in the lead chloride; and finally that 10·000 grams of lead chloride on treatment with sulphuric acid produced 10·920 grams of lead sulphate. What is the composition of lead chloride deduced from these figures?

Law of Multiple Ratios.—Lead and oxygen unite to form several compounds, each being an example of the law of fixed ratios. Berzelius, on analyzing two oxides of lead, expressed their percentage compositions as follows:—

	Lead.	Oxygen.
A.	92·85	7·15
B.	86·51	13·49

The fact that the numbers are expressed in percentages obscures a simple relation which exists between the combining ratios. This becomes apparent when the figures are recast so as to have a constant quantity of one element in both analyses, *e.g.*—

A contains $\frac{92 \cdot 85}{7 \cdot 15} = 13 \cdot 0$ of lead to 1·00 of oxygen by weight

B contains $\frac{86 \cdot 51}{13 \cdot 49} = 6 \cdot 41$ „ „ „ „

The ratio 13·0 : 6·41 is 2·03 : 1, *i.e.* the ratio of lead to oxygen is approximately twice as great in A as in B.

In all other cases, too, it is found that the quantities deduced in the above manner are connected by a simple numerical ratio, and the more rigorous the experimental conditions, the more conclusive are the results. Such results are all comprised in the **Law of Multiple Ratios or Multiple Proportions**, which may be stated as follows: **If two substances, A and B, react in more than one ratio, the various masses of A which react with a fixed mass of B bear a simple ratio to each other.**

5. Two oxides of nitrogen have the following compositions:—(i.) Nitrogen = 63·63 and oxygen = 36·36 per cent.
(ii.) Nitrogen = 46·66 and oxygen = 53·33 per cent.

Use these figures to illustrate the law of multiple proportions. (B. E. Stage I. Inorg., 1909)

6. It was found by analysis that the compounds of two elements, A and B, had the following percentage composition :—

	A	B
1st	75	25
2nd	80	20
3rd	85·7	14·3

Show how these results illustrate the law of multiple proportions. (1st Year Hons. Manc.)

7. The following are analytical figures obtained by Hilpert and Dieckmann for two arsenides of iron (*Ber.* 1911, 2378) :—

	A	B
Iron ...	27·3 per cent.	42·8 per cent.
Arsenic ...	72·82 ,,	57·79 ,,

Show how these figures illustrate the law of multiple ratios.

8. The following pairs of compounds were investigated by Berzelius, who gave the percentage compositions :—

		Sulphur.	Oxygen.
Oxides of sulphur ...	A.	40·58	59·42
	B.	50·55	49·45
		Iron.	Oxygen.
Oxides of iron	A.	69·34	30·66
	B.	77·22	22·78
		Carbon.	Oxygen.
Oxides of carbon ...	A.	28·44	71·56
	B.	44·28	55·72

Show how the law of multiple proportions holds in each case.

9. Berzelius represented the composition of copper sulphate and of basic copper sulphate as follows :—

	Copper sulphate.	Basic copper sulphate.
Copper oxide	50·9 per cent.	80·0 per cent.
Sulphuric anhydride	49·1 ,,	20·0 ,,

Show how these numbers illustrate the law of multiple ratios.

10. Discuss the following experiments of Berzelius in the light of the law of multiple proportions:—

A. The artificial sulphide of iron was prepared by direct union of the elements. 2·00 grams of this body were taken and so treated that the sulphur was first converted into sulphuric acid and then separated as barium sulphate, of which 5·38 grams were obtained. Berzelius had previously shown that barium sulphate contained 34·00 per cent. of sulphuric anhydride, and that sulphuric anhydride contained 40·58 per cent. of sulphur. The iron contained in the artificial sulphide was precipitated in the form of iron oxide (containing 69·34 per cent. of iron). From the 2·00 grams of sulphide were obtained 1·82 grams of oxide.

B. The natural sulphide of iron (pyrites), which contained a little silica as impurity, was roasted in a current of air to form the oxide. 10·00 grams of pyrites gave 6·67 grams of oxidized residue, which was found to contain 0·07 gram of silica, the remainder being iron oxide (containing 69·34 per cent. of iron).

11. Berzelius found that (*a*) 10·00 grams of copper when completely converted to black oxide gave 12·45 grams of the latter, and (*b*) 10·00 grams of black copper oxide and 10·00 grams of copper when heated in a closed vessel with hydrochloric acid left an undissolved residue of 1·97 grams of copper. Assuming that the copper oxide and copper combined to form another oxide which dissolved in the hydrochloric acid, use these figures to illustrate the law of multiple proportions.

Law of Equivalents.—Berzelius gave the percentage compositions of three substances thus—

Sulphuric anhydride.		Ferric oxide.		Ferrous sulphide.	
Sulphur ...	40·58	Iron ...	69·34	Iron ...	63·0
Oxygen ...	59·42	Oxygen ...	30·66	Sulphur ...	37·0

From the second column it is seen that the amount of oxygen which will combine with 63 parts of iron

$= 30{\cdot}66 \times \frac{63{\cdot}0}{69{\cdot}34} = 27{\cdot}8$, *i.e.* 37·0 parts of sulphur (see third column) or 27·8 parts of oxygen combine with the same amount (63 parts) of iron. These numbers, 37·0 and 27·8, are in the ratio 1 : 0·75, which is almost exactly twice the combining ratio of sulphur and oxygen in the first compound, sulphuric anhydride, for $\frac{40{\cdot}58}{59{\cdot}42} = 1 : 1{\cdot}46$.

In all such cases it is found that the ratio of the quantities of two substances which react with each other is the same as (or a simple multiple of) the ratio of the quantities which react with a third substance.

Another example.—8 grams of oxygen combine with 1 gram of hydrogen to form water, or with 23 grams of sodium to form an oxide of sodium. It has also been shown that 1 gram of hydrogen unites with 23 grams of sodium to form sodium hydride.

All such cases are comprised in the law of equivalents (sometimes called the Law of Combining Proportions, or the Law of Reciprocal Proportions), thus—

The masses of different substances A and B which react with the same mass of another substance C are either identical with, or bear a simple ratio to, the masses which will react with one another, or to the masses which will combine with a fixed mass of another substance D.

12. Illustrate the law of equivalents from the following analyses :—

Potassium chloride.		Potassium iodide.		Chloride of iodine.	
Potassium ...	52·5	Potassium	23·6	Iodine ...	78·2
Chlorine ...	47·5	Iodine ...	76·4	Chlorine ...	21·8

13. Illustrate the laws of multiple and reciprocal proportions

from the ascertained composition of the following compounds :—

Marsh gas.	Ethylene.	Carbonic oxide.	Carbonic acid.	Water.
C = 75	C = 85·71	C = 42·86	C = 27·27	H = 11·11
H = 25	H = 14·29	O = 57·14	O = 72·73	O = 88·89

(General Class, Manc.)

14. Illustrate the law of equivalents and deduce the composition of sulphuric anhydride from the following experimental data of Berzelius :—

(i.) 25·000 grams of lead gave 28·855 grams of lead sulphide.

(ii.) 25·000 grams of lead gave 26·925 grams of lead oxide.

(iii.) 30·000 grams of lead gave 43·90 grams of lead sulphate.

(iv.) 30·000 grams of lead oxide gave 40·77 grams of lead sulphate.

(v.) In experiments on the oxidation of lead sulphide it was shown that this substance may be converted into sulphate without any lead or sulphur being liberated or converted into any other substance, *i.e.* the process consists merely in the taking up of oxygen by the sulphide to form the sulphate.

Lead sulphate is formed by the direct union of lead oxide and sulphuric anhydride.

The Meaning of "Simple Ratio."—In the statement of the above laws the expression "simple ratio" has been used without any qualifying term to indicate the degree of simplicity which is implied. In general it will be found that the ratio will be capable of expression by two integers rarely greater than 5. In the case of many carbon compounds and certain mineral substances, however, ratios of greater complexity may be obtained.

Equivalents.—A slightly restricted but at the same time more useful meaning has been given to the term "equivalent." If a fixed weight of a particular element be taken as standard quantity, the equivalent of any other element is the weight which is capable of combining

with or replacing the fixed weight of the standard element. The standard usually chosen is exactly 8 units of oxygen; the equivalent of hydrogen is then 1·008, for in the commonest compound of hydrogen and oxygen, namely water, the two elements are united in the ratio of 1·008 of hydrogen to 8 of oxygen. Similarly 32·7 is the equivalent of zinc, since 32·7 parts by weight of zinc will displace 1·008 part by weight of hydrogen from sulphuric acid.

The law of multiple proportions, however, indicates the limitations of the use of equivalents. 1·008 part by weight of hydrogen is equivalent to 8 parts by weight of oxygen in the compound water; but in hydrogen peroxide it is equivalent to 16 parts by weight of oxygen. An element or group of elements may thus have several equivalents, but they will always be in the ratio of simple whole numbers. Therefore in working the following examples it must be remembered that the equivalent weights refer to the elements as present in the particular compound under consideration.

Equivalent weights of the elements, although thus restricted in use, are valuable because (i.) they express facts which are independent of any theory, and hence will not be abandoned on account of any new chemical theory that may be introduced in the future; (ii.) they are at present by far the most exact numbers from which the relative weights of the atoms are deduced with the aid of the atomic and molecular theories.

15. 5·00 grams of metallic magnesium when dissolved in hydrochloric acid evolved 0·417 gram of hydrogen. What is the equivalent of magnesium? (General Class, Manc.)

16. Calculate the equivalent of silver from the following data. 0·501 gram of silver dissolved in nitric acid gave on addition of hydrochloric acid 0·6655 gram of silver chloride. [Equivalent of chlorine is 35·46.]

(London Pre. Sci. Vet., 1905, adapted.)

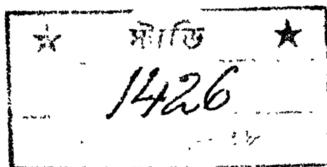
17 In a determination of the equivalent of a metal it was found that 100·0 parts by weight of it combined with 32·867 parts by weight of chlorine. Find the equivalent of the metal. (Inter. B.Sc., Manc.)

18. 1·560 grams of a liquid chloride of phosphorus were decomposed by excess of water. The resulting liquid, after adding silver nitrate, filtering, washing and drying the precipitated silver chloride, gave 4·883 grams of silver chloride. From these data calculate the equivalent of phosphorus, assuming the equivalents of silver and chlorine to be 107·9 and 35·45 respectively. (London Inter. Intl., 1909.)

19. On the assumption that the equivalent of mercury is 99·25, calculate to two places of decimals the equivalents of oxygen, hydrogen, copper, sulphur, and chlorine from the following data. Mercuric oxide contains 92·59 per cent. of mercury; cupric oxide contains 79·9 per cent. of copper; cupric chloride contains 47·3 per cent. of copper; sulphuretted hydrogen contains 94·07 per cent. of sulphur; hydrogen chloride contains 97·23 per cent. of chlorine.

(London Inter. Extl., 1907.)

20. 0·8648 gram of the black oxide of copper was so treated that there resulted 0·7781 gram of the red oxide. By a further treatment the whole of this red oxide was converted into pure copper, which weighed 0·6919 gram. What is the equivalent of copper in each compound?



CHAPTER III

THE RELATIONS BETWEEN PRESSURE, TEMPERATURE, AND VOLUME IN GASES—PARTIAL PRESSURES AND VAPOUR PRESSURES

CHEMICAL calculations are primarily concerned with the mass or quantity of matter undergoing change. The mass of a solid or of a liquid is, as a rule, quickly obtained by direct weighing, but the weighing of a gas is a more troublesome operation, and is less often carried out in practice. Once the mass of a given volume, *i.e.* the density, of a gas has been determined it is simpler, instead of weighing, to calculate the mass of another quantity of the gas from a measurement of its volume.

The volume of the gas, however, varies so considerably with alterations in pressure and temperature, that a volume measurement gives no idea of quantity unless the temperature and pressure are defined.

The variation in volume for a given change of temperature or pressure is nearly the same for all gases, so that the following general laws are almost independent of the nature of the gas, within wide limits of temperature and pressure.

Boyle's Law (or Marriotte's Law).—When a fixed quantity of gas at a constant temperature is subjected to an increased pressure, the volume decreases proportionately, and *vice versâ*. If the pressure is doubled, the volume is halved, and if the pressure is made one-tenth of

its original amount, the volume becomes ten times as great. In general, **the volume of a gas varies inversely as the pressure, provided the temperature remains unchanged.** Expressed in symbols

$$V \propto \frac{1}{P}, \quad \text{or } V = K \cdot \frac{1}{P}$$

where K is a constant; or PV = K, *i.e.* the product of the pressure into the volume is a constant quantity for the same mass of gas at a fixed temperature. In most chemical calculations the volume is measured in cubic centimetres (c.c.) and the pressure in millimetres (mm.) of mercury. For example, if 200 c.c. of air are measured at 760 mm., what will be the volume at 1000 mm., at constant temperature?

$$P_1V_1 = K = P_2V_2$$

$$760 \times 200 = 1000 \times \text{the new volume in c.c.}$$

$$\therefore \text{new volume} = \frac{200 \times 760}{1000} = 152 \text{ c.c.}$$

The student will probably find it best to argue somewhat as follows:—

$$\begin{aligned} 200 \text{ c.c. of air at } 760 \text{ mm.} &= 200 \times 760 \text{ c.c. at } 1 \text{ mm.} \\ &= \frac{200 \times 760}{1000} \text{ c.c. at } 1000 \text{ mm.} \\ &= 152 \text{ c.c.} \end{aligned}$$

The law of Boyle is only approximately true, accurate experiments showing deviations which are too large to be attributed to errors in measurement. For the calculations which appear in this and the following chapters, Boyle's law may be applied unless the contrary is expressly stated, since it is sufficiently accurate at ordinary pressures for all except the most refined measurements.

1. A gas occupies 100 c.c. at a pressure of 340 mm. of mercury. What will be the volume at pressures of 1000 mm

and 100 mm. respectively, assuming the temperature to be constant?

2. 300 c.c. of gas measured at 740 mm. pressure are passed into a vessel of 500 c.c. capacity, which has previously been evacuated. What will be the pressure in the new vessel?

3. An oxygen cylinder contains gas at a pressure of 10·3 atmospheres. It is connected with another cylinder of one-third the capacity where the pressure is 1·10 atmosphere. What will be the final pressure in the two vessels when the connecting tap is opened?

4. Three separate samples of gas each occupy 80·00 c.c. at the following pressures:—216·4, 87·2, 4·3 mm. What would be the volume of each at 760 mm. pressure?

5. A quantity of gas is collected over mercury in a tube whose open lower end stands in a reservoir of mercury. The volume of the gas is 87·0 c.c. The surface of the mercury in the tube stands 18·6 cm. higher than the surface of the mercury in the reservoir. The barometer stands at 75·4 cm. What would be the volume if the mercury were brought to the same level inside and outside the tube?

6. A volume of gas together with a crystal of rock salt measures 150·0 c.c. at 760 mm. pressure. On raising the pressure to 1000 mm. the combined volume becomes 116·4 c.c. What is the volume of the crystal?

Charles' Law (or Gay-Lussac's Law) deals with the change in volume of a fixed quantity of a gas with change in temperature. **A gas will expand $\frac{1}{273}$ (or 0·00366) of its volume at 0° Centigrade for every degree Centigrade through which it is heated, when the pressure is kept constant.** It must be noted that the fraction $\frac{1}{273}$ is dependent on the standard reference temperature of 0° C. Thus if Charles' law is applied to the convenient quantity of 273 c.c. of gas measured at 0° C., it shows that the volume at 1° C. is 273 + 1 = 274 c.c., at − 2° C. it will be 273 − 2 = 271 c.c., while at 10° C. it will be 273 + 10 = 283 c.c.

and so on, the volume at $t°$ being $273 + t$ c.c., where t may be positive or negative.

If the original volume at 0° C. was V c.c., its volume

$$\begin{array}{lll} \text{at } 1° \text{ C. would be} & V + \frac{1}{273}V \\ \text{,, } -2° \text{ C. ,,} & V - \frac{2}{273}V \\ \text{,, } 10° \text{ C. ,,} & V + \frac{10}{273}V \end{array}$$

For example, if a gas had a volume of 300 c.c. at 0° C. its volume at 10° C. would be $300 \times \frac{283}{273} = 311$ c.c.

In general, V c.c. at 0° C. become $V\left(\frac{273 + t}{273}\right)$ c.c. at $t°$. If V_o is the volume at 0° C. and V_t the volume at $t°$ C., then

$$\frac{V_t}{V_o} = \frac{273 + t}{273}$$

It will now be seen that since

$$\frac{V}{V_o} = \frac{273 + t}{273}, \text{ and } \frac{V_{t'}}{V_o} = \frac{273 + t'}{273}$$

$$\therefore \frac{V_{t'}}{V_t} = \frac{273 + t'}{273 + t}$$

EXAMPLE.—400 c.c. at 20° become at 15° C.

$$400 \times \frac{288}{293} = 393 \text{ c.c.}$$

Note.—If $t + 273$ is written T and $t' + 273 = T'$, then it is clear that T and T′ represent temperatures to which the volume is proportional. These temperatures, obtained by adding algebraically 273 to the Centigrade values, are called **absolute temperatures.** Absolute zero or − 273° C. is the temperature at which, if Charles' Law were absolutely accurate, all gases would have zero volume. This being impossible Charles' Law evidently does not apply at very low temperatures, so that the methods of correction studied above must not be expected to apply in extreme cases.

It is advisable for the student to distinguish between

such approximate laws as those of Charles and Boyle, and laws which are accurate so far as the most delicate measurements can test them, such as the law of Conservation of Mass, and the laws of Combination by Weight.

7. 208 c.c. of hydrogen were measured at a temperature of 20° C. What will be the volumes at 100°, 180°, 360°, and 500° C., the pressure being constant?

8. One sample of gas occupied 75 c.c. at 25° C., and another sample 100 c.c. at 250° C. Which would have the greater volume at 100° C., the pressure being constant?

9. A litre of gas is measured at 20° C. At what temperature will its volume be 1750 c.c.?

10. Which will show the greater expansion, 100 c.c. of gas at 0° C. heated to 20° C., or 300 c.c. at 600° C. heated to 620° C.?

Simultaneous Corrections for Temperature and Pressure—The two corrections for temperature and pressure can be applied as in the following example:—

1000 c.c. of hydrogen are measured at 100° C. and 700 mm. pressure. What would be the volume at 0° C. and 760 mm.?

1000 c.c. at 100° and 700 mm.

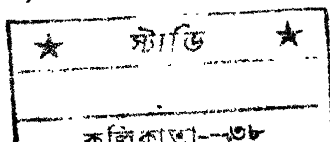
$= 1000 \times \frac{700}{760}$ at 100° C. and 760 mm.

$= 1000 \times \frac{700}{760} \times \frac{273}{373}$ at 0° C. and 760 mm.

$= 674$ c.c.

The nature of the relations between pressure, temperature, and volume for a fixed quantity of gas can be expressed by PV = constant × T, or, as it is generally written, PV = RT. This expression comprises the laws of Boyle and Gay-Lussac, as may be seen by noting that—

(i.) If T is constant, then RT is constant and PV = constant.



(ii.) If P is constant, then V = constant × T, or V is proportional to the absolute temperature.

It may further be deduced that—

(iii.) If V is constant, P = constant × T, or P is proportional to the absolute temperature.

These corrections are so often to be applied later that only a few exercises in them are given in this chapter.

Normal Temperature and Pressure.—For the comparison of different volumes of gas, measured at various temperatures and pressures, it is convenient to adopt as standards, 0° C. and 760 mm. These are called normal temperature and pressure (N.T.P.).

11. A gas measured 302·4 c.c. at 17·6° C. and 731 mm. pressure. What is its volume at N.T.P.?

12. For a given gas, P = 3·2 atmospheres, V = 22·4 litres, T = 291° absolute. What is P when V = 100 litres and the temperature is 0° C.?

13. Of two samples of hydrogen, one has a volume of 251·3 c.c. at 12° C. and 171 mm., and the other 220 c.c. at 17° and 197 mm. Which contains the greater amount of matter?

Partial Pressures and Vapour Pressure.—If a mixture of gases has a total pressure P, then P is the sum of a series of "partial pressures," $p_1 + p_2 + p_3 + \ldots$ etc. (Dalton's law). Each of these values represents the pressure which would be exerted by a single constituent gas occupying the same volume at the same temperature. For example, if a volume of air has a pressure of 760·0 mm., made up of the following partial pressures:—

Nitrogen	587·0 mm.
Oxygen	157·6 "
Water vapour...	8·0 "
Argon...	7·1 "
Carbon dioxide	0·3 "

then if all the oxygen, for instance, were removed without change of volume the total pressure would be 760·0 − 157·6 = 602·4 mm. If the water vapour were removed instead of the oxygen the pressure would be 752·0 mm. It is then evident from Boyle's Law that if the pressure had been kept at 760·0 mm. while the water was removed the volume would have decreased to $\frac{752}{760}$ of its original amount. The application of this principle is important when a gas has been measured over water because in such a case the volume is that of a mixture of the gas and water vapour. The partial pressure of water vapour in a gas in contact with water is independent of the total pressure of the gas and varies only with the temperature. If a little water is introduced into the vacuum at the top of a barometer tube at 15° C. the height of the mercury column will be reduced by 12·7 mm., unless all the water has previously been converted into vapour. The addition of a small but sufficient quantity of water to a dry gas measured at, say, 760·0 mm., will cause a similar rise in the pressure of the gas to 772·7 mm. if the volume remains constant. Consequently a given volume of gas at 760·0 mm. and 15° contains as much of the dry gas as would exist in the same volume at a pressure of 747·3 mm. (For the values of the vapour pressure of water at various temperatures see p. 146.)

EXAMPLE.—79·3 c.c. of air are measured over water at 11° and 753 mm. What would be the volume dry at N.T.P.? The vapour pressure of water at 11° is 10 mm.

The pressure of dry air at 11° is 753 − 10 = 743 mm. Therefore at N.T.P. the volume is

$$79·3 \times \frac{743}{760} \times \frac{273}{284} = 74·5 \text{ c.c.}$$

If the water contains much dissolved matter its vapour pressure will usually differ considerably from that of pure water, and must be known exactly before this correction can be made.

Note.—It is a common practice to say that 100 volumes of air (free from carbon dioxide and water vapour) contain 79 volumes of nitrogen and argon, and 21 volumes of oxygen. This is a conventional way of saying that 100 volumes of air are formed by mixing these gases in the proportions given, although each gas is spread uniformly through the mixture, so that the volume of each gas is 100 c.c. The proportions of each are better expressed as percentage pressures, or as partial pressures, of the whole.

14. A mixture of equal volumes of dry oxygen and nitrogen is collected over water at 10° C. and 750·2 mm. Calculate the partial pressures in the mixture.

15. 170 c.c. of gas are measured over water at 15° C and 720 mm. What will be the volume dry at N.T.P.?

16. 27·3 c.c. of oxygen were measured in a dry eudiometer over mercury at 0° C. and 367 mm. pressure. The gas was then transferred to a vessel standing over water, and the water was brought to the same level inside and outside the vessel. What volume would the gas occupy at 27° C. and 760 mm.?

17. Assuming dry air to be a mixture of 20·9 per cent. oxygen and 79·1 per cent. nitrogen by volume, calculate the percentage composition by volume of air saturated with water vapour at 18° C. and 760 mm.

18. The following quantities of gas are contained over mercury in separate measuring vessels:—

70·0 c.c. of hydrogen at 15° C. and 720 mm.
10·0 c.c. of oxygen at 10° C. and 700 mm.
14·0 c.c. of nitrogen at 20° C. and 760 mm.

All are mixed in another vessel at 18° C. and the volume is found to be 94·0 c.c. What is the total pressure in the vessel and the partial pressure of each constituent?

CHAPTER IV

DENSITY.—AVOGADRO'S HYPOTHESIS AND THE USE OF GASEOUS DENSITIES FOR MOLECULAR WEIGHT DETERMINATIONS

The Densities of Solids and Liquids.—The mass of unit volume of a substance is called its density. In the metric system of units this is the number of grams in 1 cubic centimetre, and since 1 c.c. of water at 4° C. weighs 1 gram, water has at this temperature a density of unity.

The volumes and densities of all substances are affected to a greater or less extent by changes of pressure and temperature, so that any statement of a density must comprise a statement of the conditions under which it was determined. A large change in pressure is necessary to produce an appreciable change in the density of a solid or liquid, so that the effect of pressure changes is usually negligible. It is otherwise with the changes brought about by change of temperature, so that in most calculations dealing with density (*e.g.* determination of refractivities) the temperature of the determination must be stated.

Relative Densities.—The ratio

$$\frac{\text{Weight of 1 c.c. of substance at } t^\circ}{\text{Weight of 1 c.c. of water at } t_1^\circ}$$

is termed the relative density of the substance at t° compared with the density of water at t_1°, and is often found

more convenient than the absolute density as defined above. It is sometimes called the specific gravity of the substance under the stated conditions of temperature, and is written, sp. gr. $t^\circ/t_\prime^\circ$, $D^{t^\circ}_{t_\prime^\circ}$, or $d\ t^\circ/t_\prime^\circ$.

For mercury $D^{15}_{4^\circ} = 13{\cdot}559$, *i.e.* 1 c.c. of mercury at 15° weighs 13·559 times as much as 1 c.c. of water at 4°. Now, since 1 c.c. of water at 15° weighs 0·99913 gram (p. 146), then for mercury

$$D^{15^\circ}_{15^\circ} = \frac{13{\cdot}559}{0{\cdot}99913} = 13{\cdot}572.$$

1. A calibration mark is to be made on the neck of a flask to indicate a content of 250 c.c. The flask having been counterpoised on a balance, what weight of water at 15·5° C. must be added so that the surface of the water shall show where the calibration mark is to be made?

2. A vessel for measuring an exact volume of a gas is filled with mercury, the whole being at 15° C. The mercury is then run out and its weight found to be 1347·82 grams. The density of mercury at 15° being 13·5590, what is the capacity of the vessel at 15°, expressed in c.c.?

3. The following are determinations of the density of acetic acid made by various observers:—

Oudemans	...	d 15°/4°	= 1·0553
Perkin	...	d 15°/15°	= 1·0568
,,	..	d 15°/15°	= 1·05704
Ramsay	...	d 20°/4°	= 1·0491
de Visser	...	d 16·6°/4°	= 1·05315
Jones ...	...	d 16·5°/4°	= 1·0534

A recent determination (Bousfield and Lowry, *J.C.S.*, 1911, 1439) gives d 18°/4° = 1·05148 and d 20°/4° = 1·04922. From the latter figures calculate the coefficient of expansion of acetic acid, and apply to the older figures, constructing a table bringing all to 18°/4° so as to indicate the degree of concordance of the whole series. [Use table of densities of water on p. 146.]

4. Given that the specific gravity of alcohol at 15° is 0·7947 referred to water at 15°, and that the specific gravity of a mixture containing 50 per cent. by weight of alcohol is 0·9188 at the same temperature, find to the nearest c.c. the contraction in volume which takes place when a litre of alcohol is added to an equal weight of water at 15°.

Application of Densities in Weighing.—It is a well-known physical principle that when a substance is weighed in a fluid (liquid or gas) the apparent weight is less than the true weight by the weight of the fluid displaced. The true weight of a body can therefore be determined directly only by weighing *in vacuo*, against weights which have been standardized *in vacuo.*

It is customary, however, when the true weight is required, to obtain it by applying a correction for the buoyancy of air to the ordinary weighings.

5. If two weights, each 50·0000 grams, one of platinum (density = 21·5) and the other of brass (density = 8·5) were placed upon the opposite pans of a balance, what would be the difference between their apparent weights in air (*a*) at 0° C., (*b*) at 20° C.? (The weight of a litre of air at 0° is 1·29 gram, at 20° 1·20 gram.)

6. 134·851 is the apparent weight in air of a quantity of silver chloride, the weights used being made of platinum and standardized in vacuo. What is the true weight of the silver chloride? (The density of silver chloride is 5·55, and of platinum 21·5. The weight of a litre of air may be taken as 1·20 gram.)

The Densities of Gases.—The weight of 1 c.c. of hydrogen at N.T.P. is 0·0000899 gram, of oxygen 0·00143. Other gases likewise give inconveniently small numbers, so for this and other reasons the densities of gases are expressed in other units than those used for solids and liquids. Since hydrogen is the lightest of all known

gases, its density has been taken as the standard, *i.e.* 1, so that Δ_{O_2} (or D_{O_2} or d_{O_2}) = 15·90 indicates that oxygen (O_2) has a density 15·90 times as great as the density of hydrogen.*

Obviously what has been said about the necessity for paying attention to the effect of changes of temperature and pressure on the densities of solids and liquids applies with much greater force to gases, since gases are subject to much greater changes in volume than are solids and liquids, under similar changes of temperature and pressure. The density of a gas is therefore expressed as the ratio

$$\frac{\text{The weight of a given volume at normal temperature and pressure}}{\text{The weight of the same volume of hydrogen at normal temp. and press.}}$$

The most accurate determinations of the weight of a litre of hydrogen at N.T.P. give 0·0899 gram, but the number 0·0900 is usually sufficiently accurate, the error thus introduced being only 1 part in 899, or about 0·1 per cent. This number 0·0900 is usually written 0·09, but it is not forgotten that its degree of accuracy is much greater than would appear from this method of expressing it.

7. Calculate the density of helium, compared with hydrogen as unity, from the following data given by Ramsay, Collie, and Travers (*J.C.S.*, 1895, **67**, 694):—

Volume of bulb ...	33·023	33·023	33·023 c.c.
Temperature ...	19·43°	17·1°	18·33° C.
Pressure ...	763·2	763·2	615·8 mm.
Weight of gas ...	0·0061	0·0060	0·0049 gram

8. A dry flask of capacity about one litre filled with air weighs 54·428 grams. Part of the air is displaced by carbon dioxide, and the weight is then 54·844 grams. On examination

* The density of air was at one time taken as unity. Since air is 14·4 times as heavy as hydrogen at the same temperature and pressure, any density expressed with air as unity can be expressed with hydrogen as unity by multiplying it by 14·4.

it is found that 610 c.c. of carbon dioxide are present. If the measurements are made at 15° and 750 mm., and the weight of a litre of air at N.T.P. is 1·29 gram, calculate the weight of a litre of carbon dioxide at N.T.P.

9. At what temperature will carbon dioxide have the same density as air has at 0° C., the pressure being the same in each case? The density at 0° C. of carbon dioxide = 21·8, of air = 14·4.

The Vapour Densities of Solid and Liquid Substances.—The densities of vapours are expressed in the same way as those of gases, *i.e.* with hydrogen as unity. The expression

$$\frac{\text{Weight of a given volume of vapour at N.T.P.}}{\text{Weight of the same volume of hydrogen at N.T.P.}}$$

is in this case not a statement of possible fact, because the vapour cannot exist at N.T.P. It is possible, however, to calculate what the numerator would be if the vapour did not condense and if it followed Boyle's and Charles' laws when brought to N.T.P. The relative densities of a large number of vapours have been determined in this way because the values obtained have considerable theoretical significance, as will be shown in the next section.

In the experimental methods used (see text-book), the volume of the vapour of a given weight of substance is measured, or an *equivalent* amount of air is displaced by the vapour, cooled, and measured at ordinary temperatures over water.

EXAMPLE.—In a Victor Meyer's apparatus, 0·1104 gram of chloroform displaced 23·2 c.c. of air measured over water at 18° and 772 mm. pressure. Vapour tension of water at 18° = 15·4 mm.

Volume of air displaced, measured dry at N.T.P.,

$$= 23{\cdot}2 \times \frac{273}{291} \times \frac{772 - 15{\cdot}4}{760} \text{ c.c.}$$

Weight of this volume of hydrogen

$$= \frac{0 \cdot 09}{1000} \times 23 \cdot 2 \times \frac{273}{291} \times \frac{772 - 15 \cdot 4}{760} \text{ gram}$$

Whence vapour density of substance

$$= \frac{0 \cdot 1104}{\frac{0 \cdot 09}{1000} \times 23 \cdot 2 \times \frac{273}{291} \times \frac{772 - 15 \cdot 4}{760}} = 56 \cdot 6$$

10. A porcelain vessel of 100 c.c. capacity was filled with a vapour at 1092° C. and atmospheric pressure, and the weight of the vapour was found to be 0·2268 gram. What is the vapour density of the substance compared with hydrogen?

(1st Year Hons., Manc.)

11. A liquid weighing 0·2457 gram displaced, in V. Meyer's apparatus, 30·0 c.c. of air measured over water at 17° C. when the barometer stood at 774·5 mm. What is the vapour density of the substance referred to hydrogen?

(1st Year Hons., Manc.)

12. In a Victor Meyer determination 0·0926 gram of a liquid gave 28·9 c.c. of gas, collected over water and measured at 16° C. and 753·6 mm. pressure. Calculate the vapour density of the liquid. (Inter. B.Sc., Manc.)

13. In a Victor Meyer determination of the vapour density of ether, 0·1036 gram of ether displaced 32·7 c.c. of air, measured over water at 12° and 749 mm. pressure. What is the vapour density of ether?

14. In a Victor Meyer determination of the vapour density, 0·1301 gram of a substance displaced 30·1 c.c. of air, measured over water at 17° and 759 mm. pressure. What is the vapour density of the substance?

Avogadro's Hypothesis and the Use of Gaseous Densities for Molecular Weight Determinations.—The densities of gases have a special significance for the chemist owing to the simple volume relationships of gases in chemical reactions. **The law of gaseous volumes (Gay-Lussac)** states

that "**When gases react they do so in simple proportions by volume, and the volume of any gaseous product is also simply related to the volumes of the reacting gases, if all the volumes are measured under the same conditions of temperature and pressure.**"

This law is not exact, for the most carefully determined combining volume ratios of gases are not precisely expressible by whole numbers but by numbers which differ slightly from whole numbers. The differences though small are greater than the possible error of these measurements, so that the law although of great importance is not rigorously accurate like the laws of chemical combination by weight. Gay-Lussac's law suggests, however, some hypothesis as to the structure of a gas, and the uniformity of the volume-temperature and volume-pressure relationships adds force to the suggestion, which is in fact met by the **hypothesis of Avogadro**. This states that **equal volumes of all gases measured under the same conditions of temperature and pressure contain equal numbers of molecules.***

It has received support from the kinetic theory, which is based on the assumptions that matter is molecular in structure and that the molecules while perfectly elastic, obey the ordinary laws of kinetics of such masses of substances as can be experimentally investigated.

The student who wishes to make the applications of the molecular and atomic theories in the following chapters must master the arguments of those theories either in the classroom or from his text-book. They are restated here in an epitomized form at the beginning of each chapter in order to indicate those portions of the text-book which are to be consulted for the description of experimental proofs and for fuller theoretical treatment.

* The molecule is the smallest part of a substance capable of independent existence.

From Avogadro's hypothesis it follows that a gas or vapour density determination leads to the molecular weight, thus—

$$\text{The density} = \frac{\text{mass of a given volume of gas}}{\text{mass of the same volume of hydrogen}}$$

$$= \frac{\text{mass of } m \text{ molecules of the gas}}{\text{mass of } n \text{ molecules of hydrogen}}$$

By Avogadro's hypothesis $m = n$, so the ratio becomes

$$\frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of hydrogen}}$$

The denominator of the fraction is equal to 2 (or more exactly 2·016) since the molecule of hydrogen contains in all probability two atoms, and the weight of each atom is taken as unity (or more exactly 1·008). Thus the relative density of a gas or vapour is equal to half $\left(\text{or } \frac{1}{2\cdot016}\right)$ of its molecular weight, and the determination of vapour densities is valuable not only for substances which are gaseous at ordinary temperatures but for all substances which can be vapourized at temperatures where measurements are possible.

15. A quantity of gas weighing 0·062 gram occupies 25 c.c. at 100° and 760 mm. What is its molecular weight?

16. An oxide of nitrogen was found to boil at 22° C. One gram of the liquid gave at 27° a light orange-coloured gas occupying 266 c.c.; on raising the temperature to 127° the gas became dark red and occupied a volume of 709 c.c.; on raising the temperature to 527° the gas became colourless and occupied a volume of 2127 c.c., the pressure being that of the atmosphere throughout the experiment. What are the vapour densities at the different temperatures, and what inferences would you draw as to the changes of the oxide? (1st Year Hons., Manc.)

17. 120 c.c. of the vapour of water weigh 0·056 gram at

180° C. and 740 mm. Show by means of these data that the molecular weight of water is approximately 18.

(London Hons. Intl., 1909.)

An important relationship between the volume occupied by a gas and its molecular weight is established as follows:—

Since 1 litre of hydrogen at N.T.P. weighs 0·09 gram

then $\frac{2 \cdot 016}{0 \cdot 09} = 22 \cdot 4$ litres of hydrogen at N.T.P. weigh 2·016 grams

and 22·4 litres at N.T.P. of a gas of density Δ weigh $2 \cdot 016 \times \Delta$ grams

i.e. M grams, where M is the molecular weight of the substance. Hence the molecular weight in grams, or the gram-molecular weight of any gas, occupies 22·4 litres at 0° C. and 760 mm.

This relationship may be used in all cases unless a high degree of accuracy is required. Note that it depends on Avogadro's hypothesis, which, as already stated, is not quite exact. Hence it is open to just the same small errors as that hypothesis. The extent of the variation is shown by the following values of the volume occupied by the gram-molecular weights of several gases (calculated from exact atomic weights, molecular weights and densities) at N.T.P.:—

Hydrogen ...	22·43 litres	Carbon dioxide	22·26 litres
Oxygen ...	22·39 „	Chlorine ...	22·05 „
Carbon monoxide	22·39 „	Methane ...	22·44 „

18. Calculate the equivalent of a metal of which 0·18 gram when dissolved in dilute sulphuric acid evolves 166·7 c.c. of hydrogen at N.T.P. (Bd. of Ed., Stage I., Inorg., 1907.)

CHAPTER V

ATOMIC WEIGHTS

Deduction of Approximate Atomic Weights from Molecular Weights.—The atom being the smallest amount of an element ever present in a molecule of any of its compounds, the atomic weight is the smallest weight of an element ever present in the molecular weight of any of its compounds. Thus the determination of the atomic weight of an element depends primarily upon a knowledge of the molecular weights of as many of its compounds as possible. If the weight of an atom of hydrogen be taken as unity a series of *approximate* molecular weights, expressed in terms of this unit, is obtained by doubling the vapour densities (see Chapter IV) of the volatile compounds of the element under consideration. For example, in the case of nitrogen :—

1	2	3	4	5
	Gas or vapour density (when hydrogen = 1).	Molecular weight (density × 2).	Per cent nitrogen in the substance.	Weight of nitrogen in molecular weight of substance.
Nitrogen	14	28	100	28
Ammonia	8·5	17	82·4	14
Hydrazoic acid ...	21·5	43	97·7	42
Nitrous oxide ...	22	44	63·6	28
Nitric oxide ...	15	30	46·7	14
Cyanogen ...	26	52	53·8	28
Ethyl nitrate	45·5	91	15·4	14
Nitrobenzene	61·5	123	11·4	14

The first column shows the compound, the second its vapour density; the third is the molecular weight deduced from the second by multiplication by 2; the fourth is the percentage of nitrogen in the compound as determined by gravimetric analysis independently of any theory; the fifth is the weight of nitrogen in the molecular weight of the compound, determined from the preceding two columns. It is evident that 14 is not only the least weight of nitrogen present in the molecular weight of any compound, but also that the compounds containing more than this have exactly 2 × 14 or 3 × 14, *i.e.* 2 or 3 atoms respectively present in the molecule. The atomic weight of nitrogen is thus 14.

In a similar way the atomic weights of oxygen and carbon are found:—

	Gas or vapour density.	Molecular weight.	Weight of oxygen in molecular weight of compound.	Weight of carbon in molecular weight of compound.
Nitrous oxide	22	44	16	—
Nitric oxide...	15	30	16.	—
Water	9	18	16	—
Ozone	24	48	48	—
Cyanogen	26	52	—	24
Carbon monoxide ...	14	28	16	12
Carbon dioxide	22	44	32	12
Carbonyl chloride ...	49 5	99	16	12

From these and from a very large number of similar determinations it is deduced that the atomic weight of oxygen is approximately 16, and of carbon 12.

If a symbol is used to represent an atom of an element, *e.g.* H for hydrogen, O for oxygen, N for nitrogen, C for carbon, then formulæ are deduced for the compounds thus—

Nitrous oxide contains 28 parts or 2 atoms of nitrogen

and 16 parts or 1 atom of oxygen. Its formula is therefore written N_2O. Nitric oxide is NO, water is H_2O, ozone is O_3, cyanogen is C_2N_2, carbon monoxide is CO, carbon dioxide is CO_2, ammonia is NH_3, and hydrazoic acid is HN_3.

Against the above as a general method of obtaining atomic weights, the following objections may be advanced:—

(1) Avogadro's hypothesis is not exactly true; hence the molecular weights obtained by its use are only approximate.

(2) The determination of vapour densities is easy when the object is an approximate value, but extraordinarily difficult when an exact value is required.

(3) Few volatile compounds of the metals are known.

For these reasons, such atomic weights as can be obtained are approximate; it is only quite recently that D. Berthelot, Guye, and others have eliminated the two sources of error (1) and (2) so as to obtain accurate atomic weights for a few elements. Nevertheless, the knowledge of the approximate value has been of service for many years as an aid to the choice of an exact atomic weight.

Exact Atomic Weights.—Since the time of Berzelius chemical analysis has indicated with considerable accuracy the equivalent weights of elements, or the ratios by weight in which they combine (Chapter II.). It is usually from these that the exact atomic weights are obtained.

The accurate combining ratio of hydrogen to oxygen in water is 2·016 : 16·00, *i.e.* their atomic weights are in the ratio 1·008 : 16·00, since the formula of water is H_2O (see above). It has recently been decided by the International Committee on Atomic Weights to fix O = 16 exactly as the standard. This means that in calculations with any

pretence to accuracy it is essential to use the value 1·008 for the atomic weight of hydrogen. If the approximate number 1 is used, as was the case in the early portion of this chapter, it must be remembered that an error of nearly 1 per cent. is thereby introduced.

From the equivalent of any other element M its atomic weight may be deduced as follows. The element may combine with oxygen to form some of the oxides—



$$M_2O \quad MO \quad M_2O_3 \quad MO_2 \quad M_2O_5 \quad MO_3 \quad M_2O_7 \quad MO_4$$

The atomic weight, A, of the element combines with the following weights of oxygen respectively:—

$$8 \quad 8\times2 \quad 8\times3 \quad 8\times4 \quad 8\times5 \quad 8\times6 \quad 8\times7 \quad 8\times8$$

Hence the equivalent of the element, *i.e.* the amount which combines with 8 parts by weight of oxygen, is—

$$A \quad \frac{A}{2} \quad \frac{A}{3} \quad \frac{A}{4} \quad \frac{A}{5} \quad \frac{A}{6} \quad \frac{A}{7} \quad \frac{A}{8}$$

If these oxides are assumed to be formed from water by the displacement of the hydrogen atoms by atoms of M, then in the eight compounds one atom of metal has replaced the following number of atoms of hydrogen (cf. formulæ), 1, 2, 3, 4, 5, 6, 7, 8. This number is the **valency** of the element. (See text-book for fuller discussion of this all-important subject.) It coincides with the denominator in the line A, $\frac{A}{2}, \frac{A}{3}$, etc.

Hence $\quad \text{Equivalent} = \dfrac{\text{atomic weight}}{\text{valency}}$

i.e. **Atomic weight = valency × equivalent.**

Since the valency is a simple whole number (from 1 to 8), and the equivalent is accurately known, the atomic weight is chosen by trial as that number which is nearest the approximate one as determined above, when in the formula is substituted for valency the numbers 1, 2, 3 . . . 8 in turn.

EXAMPLE.—A metallic chloride was found to contain 25·60 per cent. of chlorine. What would be the atomic weight of the metal on the supposition that it was (*a*) a diad, (*b*) a triad? (Cl = 35·46.) (Inter. B.Sc., Manc.)

"Diad" and "triad" are terms sometimes used for divalent and trivalent elements respectively.

25·60 of chlorine unite with 100 − 25·60 of metal
i.e. 74·40 of metal

$$\therefore 74{\cdot}40 \times \frac{35{\cdot}46}{25{\cdot}60} \text{ of metal unite with } 35{\cdot}46 \text{ of chlorine}$$

i.e. 103·06 of metal unite with 35·46 of chlorine, or replace 1·008 of hydrogen in hydrochloric acid.

Hence since atomic weight = equivalent × valency
then the atomic weight = (*a*) 103·06 × 2 = 206·1
or (*b*) 103·06 × 3 = 309·2

Approximate Atomic Weights obtained by the Use of Dulong and Petit's Generalization.—Only a few elements have a sufficient number of volatile compounds for the determination of their approximate atomic weights from vapour density observations. For most elements an independent rule or generalization enunciated by Dulong and Petit may be applied. This states that the product of the atomic weight and the specific heat (measured at ordinary temperatures) of a solid or liquid element is a constant, approximately 6·4. This generalization holds particularly for those elements which form the fewest volatile compounds, and whose atomic weights are thus least easy to determine by the previous method. The notable exceptions to Dulong and Petit's generalization are beryllium (glucinum), boron, carbon, and silicon, whose atomic weights have been determined by the previous method.

It is especially important to note that the value of the atomic weight obtained from the equation—

$$\text{Atomic weight} \times \text{specific heat} = 6{\cdot}4$$

is only very approximate, so that the exact number must be obtained from the equation—

$$\text{Atomic weight} = \text{valency} \times \text{equivalent}$$

EXAMPLE.—A metallic oxide was found to contain 52·94 per cent. of the metal and 47·06 of oxygen. A rapid determination of the specific heat of the metal gave 0·25. What is the exact atomic weight of the metal (O = 16), and what is the formula of the oxide?

52·94 of metal combine with 47·06 of oxygen

$$\therefore \frac{52 \cdot 94}{47 \cdot 06} \times 8 \quad \text{,,} \quad \text{,,} \quad 8 \quad \text{,,}$$

$$\textit{i.e.}\ \text{equivalent of metal} = \frac{52 \cdot 94}{47 \cdot 06} \times 8$$
$$= 9 \cdot 00$$

Also, from Dulong and Petit's generalization—

$$\text{Atomic weight} \times 0 \cdot 25 = 6 \cdot 4 \text{ approximately}$$
or, $$\text{Atomic weight} = 25 \cdot 6 \text{ approximately.}$$

Now, atomic weight = valency × 9·00, and adopting values for the valency, in turn, of 1, 2, 3, and so on—

$$\text{Atomic weight either} = 1 \times 9 \cdot 00 = 9 \cdot 00$$
$$\text{or} = 2 \times 9 \cdot 00 = 18 \cdot 00$$
$$\text{or} = 3 \times 9 \cdot 00 = 27 \cdot 00$$
$$\text{or} = 4 \times 9 \cdot 00 = 36 \cdot 00 \text{; and so on.}$$

Since 27·00 is nearest the approximate number 25·6, the exact atomic weight is 27·00, the valency is 3, and the formula for the oxide is M_2O_3.

For atomic weights required in the following examples, see p. 147.

1. By the action of hydrochloric acid on 0·1635 gram of a metal, 56 c.c. of hydrogen measured at N.T.P. were obtained. Calculate the atomic weight of the metal assuming the chloride to have the formula MCl_2. (B.Sc., Manc.)

2. A metallic oxide is found to contain 21·33 per cent. of

oxygen. The specific heat of the metal is found to be 0·055. What is the exact equivalent of the metal, and what is its probable atomic weight? (General Class, Manc.)

3. A metallic oxide was found to contain 48·0 per cent. of oxygen. What is the exact equivalent of the metal? If the specific heat of the metal was found to be 0·123, what is the probable atomic weight and valency of the metal, and what would be the probable nature of the oxide?

(Inter. B.Sc., Manc.)

4. An oxide of a metal contains 20 per cent. of oxygen, and forms salts with acids. What are the possible formulæ and molecular weights which could be assigned to the oxide? If the specific heat of the metal was found to be 0·098, which of these molecular weights would you accept?

(Inter. B.Sc., Manc., 1906.)

5. The specific heat of a metal was found to be 0·237, and the chloride of this metal was found to contain 80·0 per cent. of chlorine. What is the atomic weight of the metal, and the formula of the chloride? (Cl = 35·5.)

(General Class, Manc.)

6. 2·380 grams of tin gave by treatment with concentrated nitric acid and subsequent ignition 3·020 grams of oxide. The specific heat of tin is 0·054. From these data calculate the equivalent and the atomic weight of this element.

(Sch. of Technology, Manc., 1st Year.)

7. On dissolving 0·444 gram of a metal in dilute sulphuric acid, 177 c.c. of hydrogen at 10° and 750 mm. were obtained. The specific heat of the metal was 0·107. Calculate its atomic weight. (London Inter., Intl., 1907.)

8. One cubic centimetre of carbon disulphide (sp. gr. = 1·29) is transformed into vapour at the boiling point of water. What volume would it occupy in these circumstances, the pressure being normal? (Inter. B.Sc., Manc.)

9. The following figures were obtained by Nilson and Pettersson in a determination of the vapour density of germanium chloride.

Volume of gas corrected to N.T.P.	6·24	11·61	4·37 c.c.
Weight of gas	0·0601	0·1121	0·0421 gram

Calculate the molecular weight of the chloride and compare it with that corresponding with the formula $GeCl_4$.

10. An element combines with fluorine to form a fluoride containing 83·8 per cent. of fluorine. The fluoride forms with hydrogen fluoride a monobasic acid. The specific heat of the element at 50° C. was found to be 0·24, and at 250° the specific heat was found to be 0·37. What is the equivalent weight of the element and what is its probable atomic weight?

(1st Year Hons., Manc.)

In many cases the formula of a compound is established, and the exact atomic weight of an element in it is determined by observation of some chemical change which the compound undergoes. The atomic weights of the other elements present must be known.

EXAMPLE.—Ammonium alum $(NH_4)_2Al_2(SO_4)_4.24H_2O$, on heating decomposes so that all the constituents except alumina are volatilized. Mallet (*Phil. Trans.*, 1880) found that 8·2144 grams of the alum gave 0·9258 gram of alumina. The atomic weight of aluminium is deduced from these figures thus—


$(NH_4)_2Al_2(SO_4)_4.24H_2O$ produces Al_2O_3

$\therefore$ 852·75 + $2x$ of alum produce 48·00 + $2x$ of alumina, where x is the atomic weight of aluminium.

$$\therefore \frac{852{\cdot}75 + 2x}{48{\cdot}00 + 2x} = \frac{8{\cdot}2144}{0{\cdot}9258}$$

whence $x = 27{\cdot}11$.

11. On drying, 6·905 grams of crystallized borax left 3·652 grams of anhydrous borax; calculate from these data the atomic weight of boron assuming the formula of crystallized borax to be $Na_2B_4O_7,10H_2O$, and that Na = 23·05, O = 16, H = 1·008. What will it be if H = 1 be taken as the standard?

(London B.Sc. Pass, Extl., 1904.)

12. When a quantity of potassium bromaurate was heated, 3·679 grams of gold and 2·219 grams of potassium bromide were obtained. Calculate the atomic weight of gold, the specific heat of the metal being 0·0324. (K = 39·10, Br = 79·92.) (B.Sc., Manc.)

13. Guye and Ter-Gazarian have recently discovered that the most carefully recrystallized potassium chlorate contains at least 0·022 per cent. of potassium chloride. Taking account of this correction recalculate the atomic weight of silver from the following data of Stas. Percentage of oxygen in potassium chlorate = 39·154. Ratio of silver to potassium chloride = 100 : 69·1143. (O = 16.) (B.Sc. Hons., Manc.)

14. Harcourt and Baker (*J.C.S.*, 1911, **99**, 1312) determined the atomic weight of tellurium by converting it into the tetra-bromide ($TeBr_4$). Calculate atomic weights from the following data :—

Weight of Tellurium.	Weight of Bromine combined
0·87822	2·20103
0·59706	1·49640
0·69189	1·73442
0·62732	1·57254
0·58307	1·46162

15. According to Stas' determinations—

$KClO_3$ contains 39·19 per cent. of oxygen.
100 grams Ag are precipitated by 69·1 grams KCl.
100 grams Ag form 132·85 grams AgCl.

From these data calculate the atomic weight of chlorine. (1st Year Hons., Manc.)

16. It has been found, when one gram of hydrogen is burnt in excess of chlorine over water, that 35·288 grams of chlorine dissolve in the water as hydrochloric acid, and that 14 c.c. of oxygen are liberated from the aqueous vapour. What is the atomic weight of chlorine from this experiment? (1st Year Hons., Manc.)

17. According to Stas, when carbon monoxide is passed

over heated copper oxide, 2·750 grams of carbon dioxide are formed for every gram of oxygen lost by the copper oxide. According to Leduc the density of carbon monoxide is 13·92 compared with hydrogen. What values for the atomic weight of carbon would you calculate from these determinations if H = 1·008? (1st Year Hons., Manc.)

18. The percentage composition of rubidium alum is Al_2O_3, 9·81; SO_3, 30·73; Rb_2O, 17·95; H_2O, 41·51. The composition of another alum containing an element M is M_2O_3, 13·30; SO_3, 29·53; Rb_2O, 17·29; H_2O, 39·88. Calculate the atomic weight of the element M, if Al = 27·1 and Rb = 85·5. (Lond. B.Sc., 1906.)

19. 1·0000 gram of calcite containing 1·00 per cent. of iron heated in air yields 0·5620 of residue; determine the combining weight of calcium (Fe = 56, C = 12, O = 16.) [Assume iron present as $FeCO_3$.]

(B.Sc., Manc.)

20. 1000 c.c. of mercury vapour at N.T.P. weigh 8·923 grams. [Assume that mercury vapour can exist at 0° and 760 mm. without condensation.] 118·394 grams of mercuric oxide yield when heated 109·63 grams of mercury. Assuming mercuric oxide is formed by the union of one atom of mercury with one atom of oxygen, what light do these data throw on the atomic and molecular weights of the metal?

(Final, Manc., 1911, adapted.)

21. If we suppose that in Dumas' determination of the combining weights of oxygen and hydrogen, for every 18·016 grams of water formed, 0·0044 gram of CO_2 was produced owing to the presence of marsh gas in the hydrogen used, what value would have been found for the atomic weight of hydrogen?

22. In Dumas' experiment on the combining weights of oxygen and hydrogen: if, for every 2·016 grams of hydrogen burnt by the copper oxide, 0·0016 gram of sulphur dioxide (carried over from the sulphuric acid drying tubes) had been decomposed in the heated bulb, what weight of water would

have been collected, and if the sulphur had all combined with the copper what effect would the impurity have had on the atomic weight determination?

[The last two calculations have been adapted from Manchester examination questions, to suit the more modern atomic weights.]

CHAPTER VI

PERCENTAGE COMPOSITIONS FROM FORMULÆ AND FORMULÆ FROM PERCENTAGE COMPOSITIONS

Deduction of Percentage Compositions from Formulæ using Atomic Weights.—One of the consequences of the atomic theory is the representation of chemical compounds by means of formulæ composed of symbols of the elements. A knowledge of atomic weights enables the proportions (by weight) of the elements to be deduced from these formulæ. Thus H_2O, the formula for water, represents a compound containing 2·016 parts of hydrogen to 16·00 parts of oxygen by weight, or 88·8 per cent. of oxygen and 11·2 per cent. of hydrogen.

For convenience the proportions are generally expressed in percentages, which are calculated by simple proportion. The composition of potassium ferricyanide, [$K_3Fe(CN)_6$], for instance, is deduced as follows:—

$$\begin{aligned}\text{Weight of molecule} &= \text{sum of weights of the atoms in it}\\ &= (3\times 39)+56+(6\times 12)+(6\times 14)\\ &= 329\end{aligned}$$

These 329 parts of $K_3Fe(CN)_6$ contain 3×39 parts of potassium, so that—

$$\text{Percentage of potassium} = \frac{3\times 39}{329}\times 100 = 35{\cdot}6$$

Similarly—

$$\text{Percentage of iron} = \frac{56}{329} \times 100 = 17{\cdot}0$$

$$\text{Percentage of carbon} = \frac{6 \times 12}{329} \times 100 = 21{\cdot}9$$

$$\text{Percentage of nitrogen} = \frac{6 \times 14}{329} \times 100 = 25{\cdot}5$$

It has been shown in Chapter II., Example 9, that Berzelius represented copper sulphate as a compound of copper oxide and sulphuric anhydride. This method of resolving the formulæ of complex compounds into simpler molecules is often used to indicate the chemical character more clearly, *e.g.*—

Red lead, Pb_3O_4, is $2PbO, PbO_2$.

Potassium hydrogen sulphate, $KHSO_4$, is $K_2SO_4.H_2SO_4$ [*i.e.* $2KHSO_4$].

Malachite, $Cu_2H_2CO_5$, is $Cu(OH)_2.CuCO_3$, or $2CuO.CO_2.H_2O$.

Mica, $KAl_3H_2Si_3O_{12}$ [$KAl_3H_2(SiO_4)_3$], is $K_2O.3Al_2O_3.2H_2O.6SiO_2$.

Boracite, $Mg_7Cl_2B_{16}O_{30}$, is $MgCl_22Mg_3B_8O_{15}$, or $MgCl_2.6MgO.8B_2O_8$.

In each of these cases there is a choice of the terms in which the percentage composition may be expressed.

It is, of course, also possible to represent formulæ, and to express percentage compositions in terms of the radicles present. Thus malachite (above) may be written $Cu_2(OH)_2CO_3$, and its composition may be expressed as percentages of Cu, OH, and CO_3.

EXAMPLES.—**Find the percentage elementary compositions of two or three of the following, as accurately as possible, using International Atomic Weights (p. 147).**

1. Potassium carbonate, K_2CO_3.

2. Hydrogen peroxide, H_2O_2.

3. Ferric chloride, $FeCl_3$ or Fe_2Cl_6.

4. Nitrosyl chloride, NOCl.

5. Cryolite, $AlF_3.3NaF$ or Na_3AlF_6.

6. Ammonium platinichloride, $(NH_4)_2PtCl_6$.

7. Ethyl nitrite, $C_2H_5NO_2$.

8. Ethyl acetoacetate, $CH_3.CO.CH_2COOC_2H_5$.

9. Sodium benzene sulphonate, $C_6H_5SO_3Na$.

10. Express the percentage composition of malachite in terms of CuO, CO_2, and H_2O.

11. Express the percentage composition of kaolin, ($H_2Al_2Si_2O_8.H_2O$), in terms of Al_2O_3, SiO_2, H_2O ("constitutional"), H_2O ("hydration").

12. Express the percentage composition of crystallized sodium carbonate, $Na_2CO_3.10H_2O$, in terms of anhydrous sodium carbonate and water of crystallization.

13. Adie (*J.C.S.*, 1900, **77**, 1076) gave the composition of a potassium sodium cobaltinitrite as follows:—

K = 17·2	Co = 13·1
Na = 4·9	NO_2 = 61·2

H_2O = 4·1

Compare this with the numbers calculated from the formula $K_2NaCo(NO_2)_6.H_2O$.

14. 0·0930 grams of a substance believed to have the formula $C_{17}H_{24}O_5N_2.HAuCl_4$ was ignited, and left a residue of 0·0272 grams of pure gold (Power and Callan, *J. C. S.*, 1911, **99**, 2000). Show that these analytical figures agree with the formula assigned to the compound.

15. A substance was found to contain 30·12 per cent. of barium. Which of the following two formulæ expresses the composition more nearly: $(C_8H_{13}O_3)_2Ba$ or $(C_8H_{15}O_3)_2Ba$?

(Smedley, *J.C.S.*, 1911, **99**, 1632.)

Deduction of Formulæ from Percentage Composition, using Atomic Weights.—The method of constructing a formula to correspond with a given percentage composition may be deduced by considering a definite case. D. Berthelot obtained the following figures on analyzing a compound containing mercury, nitrogen, and iodine:—

Mercury = 73·77
Nitrogen = 2·53
Iodine = 23·56

These quantities may each be resolved into two factors, one being the atomic weight of the element under consideration, thus—

Mercury = 73·77 = 0·369 × 200
Nitrogen = 2·53 = 0·181 × 14
Iodine = 23·56 = 0·185 × 127

[The fractional numbers are found by dividing the percentage of each element by its atomic weight.]

The numbers 0·369, 0·181, and 0·185, are approximately in the ratio of the numbers of atoms present; they must be transformed into simple whole numbers, since fractions of atoms are never found in chemical compounds.

They are clearly very nearly as 2 : 1 : 1, and the simplest, or empirical, formula of the compound is Hg_2NI.*

* A more precise proof runs as follows: If the elements A, B, C, form a compound $A_pB_qC_r$, and if the atomic weights of A, B, and C are a, b, and c, then the total weight of the molecule of the compound is $pa + qb + rc$.

$$\text{The percentage of A} = \frac{100\,pa}{pa + qb + rc}$$

$$\text{The percentage of B} = \frac{100\,qb}{pa + qb + rc}$$

$$\text{The percentage of C} = \frac{100\,rc}{pa + qb + rc}$$

The problem is, to determine p, q, and r, given the percentages of the elements, and a, b, and c.

It is not possible, of course, to decide without further information between this formula and some simple multiple of it, *e.g.* $Hg_4N_2I_2$ or $Hg_6N_3I_3$.

If the analysis is expressed in percentages of simpler compounds the process is similar—

$$\begin{aligned} \textit{e.g. } SiO_2 &= 47{\cdot}0 = 0{\cdot}78 \times 60 \; (SiO_2 = 28 + 32 = 60) \\ MgO &= 31{\cdot}3 = 0{\cdot}78 \times 40 \; (MgO = 24 + 16 = 40) \\ H_2O &= 21{\cdot}2 = 1{\cdot}18 \times 18 \; (H_2O = \;\; 2 + 16 = 18) \end{aligned}$$

99·5 per cent.

0·78 : 0·78 : 1·18 = 2 : 2 : 3 very nearly, and the formula is $2MgO.2SiO_2 3H_2O$, or $2MgSiO_3.3H_2O$.

Since the usual analytical data for determining the composition of a compound are less accurate than the data from which the atomic weights are obtained, the proportions deduced are rarely quite exact. For this reason approximate atomic weights may be used in deducing formulæ from analytical data.

The procedure to be followed in determining the formula of a body from its percentage composition is therefore—

(1) **Divide each percentage by the corresponding atomic (or group) weight to obtain the ratio of the number of atoms (or groups) present.**

Now per cent. of A : per cent. of B : per cent. of C

$$= \frac{100\,pa}{pa + qb + rc} : \frac{100\,qb}{pa + qb + rc} : \frac{100\,rc}{pa + qb + rc}$$
$$= pa : qb : rc$$

Whence $\dfrac{\text{per cent. of A}}{a} : \dfrac{\text{per cent. of B}}{b} : \dfrac{\text{per cent. of C}}{c} = p : q : r$

Hence the proportion of the numbers of atoms present ($p : q : r$) is obtained by dividing each percentage by the corresponding atomic weight. Multiplication of the result by some constant number transforms these proportions into the simple whole numbers which show the empirical formula of the body.

(2) Find the simplest whole numbers to express this ratio. If these are not obvious, divide each by the smallest and the ratio will then be apparent.

16. An oxide of iron was found by analysis to have the following composition: Iron = 77·7, oxygen = 22·3. Find the simplest formula and explain fully each step taken in the calculation. (Fe = 56.) (General Class, Manc.)

17. A solid hydrocarbon was found to contain 93·75 per cent. carbon and 6·25 per cent. hydrogen. Its vapour density was 64. What formula would you assign to the substance? (Inter. B.Sc., Manc., 1910.)

18. A mineral contains—

Sodium	... ...	32·79 per cent.
Aluminium	... ...	13·02 „ „
Fluorine	... ...	54·19 „ „

Calculate its simplest formula, using the following atomic weights: Na = 23·05, Al = 27·1, F = 19.

Give the details of your calculations.

(Bd. of Ed., Stage II., Inorg., 1905.)

19. A double carbonate of nickel and potassium gave the following analytical data. (Reynolds, *J.C.S.*, 1898, 264.) What is its formula?

CO_2 ...	26·68 per cent.	K_2O ...	28·82 per cent.
NiO ...	22·64 „ „	H_2O ...	21·86 „ „

20. Find the simplest formula of a substance with the following percentage composition:—

Copper ...	29·86 per cent.	Nitrogen ...	13·27 per cent.
Sulphur ...	15·17 „ „	Oxygen ...	37·91 „ „
	Hydrogen ...	3·79 per cent.	

21. A mineral is found to contain, in addition to oxygen, 5·1 per cent. of beryllium, 10·2 per cent. of aluminium, and 31·2 per cent. of silicon; determine its simplest formula, and show how beryllium sulphate may be prepared from it. (O = 16, Be = 9·1, Al = 27·1, Si = 28·4.)

(2nd Year Hons., Manc., 1910.)

22. The insoluble $Cd(NH_4)PO_4.H_2O$ (stable at 100°) on ignition gives cadmium pyrophosphate, $Cd_2P_2O_7$. A solution of a cadmium salt gave 0·4530 gram of the hydrated salt and 0·3712 gram of the pyro salt. How much cadmium was present? (Miller and Page, *Chem. News*, 1901, 313.)

23. An analysis of a mineral gave the following results :—

Silica ...	57·54 per cent.	Lime ...	8·95 per cent.
Alumina	16·28 " "	Water ...	17·23 " "

What is the simplest formula for a mineral of this composition? (Si = 28, Al = 27, Ca = 40, H = 1, O = 16.)

(B.Sc., Manc., 1911.)

24. The following is an analysis by Brauner (*J.C.S.*, 1898, 958) of a double oxalate of thorium and ammonium. What is its formula?

ThO_2	33·81 per cent.
C_2O_3 (oxalic anhydride)	36·89 " "
$(NH_4)_2O$	13·39 " "
H_2O	16·11 " "

25. Müller and Diefenthaler (*Ber.* 1910, 2322) give the following analysis of a salt prepared by treating lead nitrate with potassium ferricyanide :—

Pb = 52·86	$Fe(CN)_6'''$ = 27·07
NO_3 = 7·69	H_2O = 11·61

with the following confirmatory data :—

Fe = 7·27	C = 9·23

What is the formula of the compound? Show that the confirmatory data agree with the formula.

26. The following figures are taken from an analysis by Werner (*J.C.S.*, 1888, 404) of a *basic* double oxalate of potassium and chromium. Suggest a formula for the substance.

Potassium	24·00 per cent.
Chromium	16·22 " "
Oxalate radicle (C_2O_4)	54·39 " "

27. Debus (*J.C.S.*, 1888, 288) gave the following analysis

of the hydrated potassium salt of a thionic acid. What is the probable formula of the compound?

Potassium	... ...	21·64 per cent.
Sulphur	... ...	43·97 „ „
Water of hydration	...	7·81 „ „

28. Find the formula of the hydrated mercuric potassium nitrite of which the following is a partial analysis. (Rây, *J.C.S.*, 1907, **91**, 2032.)

Hg ... 35·19 per cent. K ... 20·24 per cent.
N ... 12·00 per cent.

29. The percentage composition of chloride of silicon has been ascertained to be—

Si = 16·47 per cent. Cl = 83·53 per cent.

Its vapour density is 85 (H = 1). Assuming Cl = 35·5, calculate from these data the atomic weight of silicon.

(Inter., Manc., 1910.)

[N.B.—It is necessary to assume that silicon chloride contains only one atom of silicon.]

Analysis of Minerals.—In certain minerals one element may often replace another to any extent without altering the crystalline form of the mineral. These so-called isomorphous relationships are expressed by writing the symbols of both elements and enclosing them in a square bracket, *e.g.* olivine is $[Mg, Fe]_2.SiO_4$, or $2[Mg, Fe]O.SiO_2$, indicating that the mineral is of the type Mg_2SiO_4 with more or less of the Mg replaced by Fe. It is of course impossible to calculate a percentage composition for olivine unless the proportions of magnesium and iron are definitely stated.

The deduction of formulæ for such minerals is carried out on the lines of the following determination for dolomite:—

CaO	...	31·37 = 0·560 × 56
MgO	...	21·23 = 0·525 × 40
CO_2	...	47·67 = 1·083 × 44

Here the relations between the numbers are not simple,

but the CaO and the MgO are together equal to 1·085, which corresponds closely with the figure for CO_2, so that the formula may be written, [CaO, MgO]CO_2, or [Ca, Mg]CO_3.

Another instance of isomorphous replacement is found in an analysis of soda felspar :—

SiO_2	...	68·45 ÷ 60 = 1·141
Al_2O_3	...	18·71 ÷ 102 = 0·183
Fe_2O_3	...	0·27 ÷ 160 = 0·0016
CaO	...	0·50 ÷ 56 = 0·009
MgO	...	0·18 ÷ 40 = 0·0045
K_2O	...	0·65 ÷ 94 = 0·007
Na_2O	...	11·24 ÷ 62 = 0·181

In this case the relationships are not so exact and the analysis is not that of a pure substance. But arguing that the lime and magnesia are combined with 0·0135 (*i.e.* 0·009 + 0·0045) silica, then 0·188 molecule of [NaK]$_2$O and 0·185 of [AlFe]$_2O_3$ are combined with 1·1275 of SiO_2. These figures agree with the formula $Na_2O.Al_2O_3.6SiO_2$, or $NaAlSi_3O_8$.

30. The following are two analyses of spinel. What is its formula?

Al_2O_3	isomorphous	67·75	...	60 79
Fe_2O_3	isomorphous	2·88	...	5·26
FeO	isomorphous	0·86	...	21·74
MgO	isomorphous	27·04	...	12·84

31. Cabrerite (Sachs, *J.C.S.*, 1906, **90**, 369) gave on analysis—

	As_2O_5	= 40·45
Isomorphous	NiO	= 26·97
Isomorphous	FeO	= 1·10
Isomorphous	MgO	= 6·16
	H_2O	= 25·26
	Total	= 99·94

Find a formula for this mineral.

32. Natrolite (Harrington, *J C.S.*, 1906, **90**, 867), gave on analysis—

SiO_2 =	47·09
Al_2O_3 =	26·99
Na_2O =	16·46
K_2O =	0·01
H_2O =	9·80
Total =	100·35

Find a formula for this mineral.

33. Deduce the formula of the mineral wolframite from the following analysis by Finlayson (*J.C.S.*, 1910, **98**, 308).

WO_3 ...	76·24	MnO ...	6·05
FeO ...	16·39	CaO ...	1·05
MgO ...	0·11		

34. Deduce the formula of the mineral datolite from the following analysis by Fromme (*J.C.S.*, 1910, **98**, 314):—

CaO ...	34·91	B_2O_3 ...	20·79
SiO_2 ...	37·65	Al_2O_3 ...	1·18
H_2O ...	5·90		

It must be noted that only the salts of the so-called oxyacids can be resolved into two oxides for the purpose of expressing their composition. It is not possible to represent calcium chloride, for instance, as a compound containing calcium oxide together with an anhydride of hydrochloric acid. As the total amount of metal found in a mineral is usually represented in the percentage composition by the equivalent quantity of its oxide, and as the amount of a halogen is generally expressed as the percentage of the element, it is clear that the composition as put in this way will not be a true percentage composition since the sum will exceed 100 by the weight of oxygen wrongly attributed to the metal. The analysis of

apatite which has the formula $Ca_5(PO_4)_3Cl$, or $9CaO.$-$3P_2O_5.CaCl_2$, might be expressed as—

CaO	...	53·8	Corresponding to, though not
P_2O_5	...	40·9	actually contained in, 100
Cl	...	6·8	parts of apatite.
	Total	101·5	

If from this total is subtracted the amount of oxygen equivalent to the chlorine found (*i.e.* 1·5), which would be the amount wrongly associated with calcium, the total is exactly 100, and therefore analyses of minerals containing halogen are often corrected by subtracting from the sum of the percentages found, a quantity which is described as "O for F" or "O for Cl."

35. An analysis of sodalite was given as follows: silica = 37·1, alumina = 31·7, soda (Na_2O) = 25·5, chlorine = 7·3 per cent. Deduce the formula of the mineral. (Si = 28, Al = 27, Na = 23, Cl = 35·5.)

36. A substance which contained zinc, phosphorus, oxygen, and chlorine, gave on analysis (Basset and Taylor, *J.C.S.*, 1911, 1408)—

ZnO	...	21·24	per cent.
P_2O_5	...	36·45	" "
Cl	...	54·61	" "
	Total	112·30	" "

Find its formula.

37. Deduce the formula of the mineral cuspidine from the following analysis by Palache (*J.C.S.*, 1910, **98**, 219):—

SiO_2	...	32·36	F	...	9·05
MnO	...	0·71	Na_2O	...	0·48
CaO	...	61·37	K_2O	...	0·27

CHAPTER VII

THE CALCULATION OF REACTING QUANTITIES FROM EQUATIONS

THE construction of chemical formulæ in accordance with the atomic and molecular hypotheses leads to the representation of chemical reactions by means of equations. For example—



$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

represents the reaction between zinc and sulphuric acid under certain conditions. The quantities of the four substances concerned in the reaction are calculated from the equation by the use of a table of atomic weights. It follows that 65·37 grams of zinc will react with 98·086 grams of sulphuric acid to produce 2·016 grams of hydrogen and 161·44 grams of zinc sulphate (anhydrous).* If it were necessary to determine the weight of zinc which could be dissolved in exactly 7 kilograms of 10·00 per cent. sulphuric acid the process would be—

7000 grams of 10 per cent. acid contain 700 grams hydrogen sulphate; 98·086 grams hydrogen sulphate require 65·37 grams zinc; (from the equation)

$$\therefore \text{ 700 grams hydrogen sulphate require } \frac{65{\cdot}37 \times 700}{98{\cdot}086}$$

$$= 466{\cdot}5 \text{ grams zinc.}$$

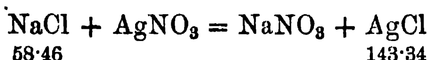
The student should repeat this calculation, using

* These figures should be checked.

approximate atomic weights (H = 1, Zn = 65, S = 32) in order to see the nature of the error introduced by so doing.

This type of calculation forms the basis of ordinary gravimetric analysis, as will be seen from the following example :—

A solution of sodium chloride gave with silver nitrate a precipitate of 0·2543 gram of silver chloride. How much sodium chloride was present in the solution ?



$$\underset{58{\cdot}46}{NaCl} + AgNO_3 = NaNO_3 + \underset{143{\cdot}34}{AgCl}$$

i.e. 143·34 grams of silver chloride result from 58·46 grams of sodium chloride ;

$$\therefore 0{\cdot}2543 \text{ gram of silver chloride results from } \frac{58{\cdot}46 \times 0{\cdot}2543}{143{\cdot}34}$$

$$= 0{\cdot}1037 \text{ gram of sodium chloride.}$$

For the following exercises, use the International Atomic Weights (p. 147) unless approximate values are given, or unless the data render the use of exact values of no gain to the accuracy of the calculation.

1. How much potassium chlorate must be heated to yield as much oxygen as would be obtainable from 500 grams of mercuric oxide? (K = 39, Cl = 35·5, O = 16, Hg = 200.)
(Bd. of Ed., Stage I., Inorg., 1904.)

2. What products would be obtained, and what weight of each, when 10 grams of (*a*) potassium chlorate, and of (*b*) white marble are separately heated to redness until no further change occurs ? (K = 39, Cl = 35·5, Ca = 40, C = 12, O = 16.)
(Bd. of E., Stage I., Inorg., 1905.)

3. How much anhydrous sodium carbonate should theoretically be obtained from 100 lbs. of salt cake ?

4. 100 c.c. of a solution of sulphuric acid was exactly neutralized by 32·0 grams of anhydrous sodium carbonate.

Express the composition of the acid solution in terms of grams of sulphuric acid per litre. (Na = 23, C = 12, O = 16, S = 32, H = 1.) (Manchester Sch. of Tech., 1st Year, 1911.)

5. On passing pure carbon monoxide over heated copper oxide it was found that the loss in weight was 24·360 grams, and that the amount of carbon dioxide formed was 67·003 grams. From these data calculate the equivalent of carbon when O = 16. (Bd. of Ed., Stage II., Inorg., 1907.)

6. A solution of hydrobromic acid has a density of 1·055; 10 c.c. of this gave 1·878 gram of silver bromide; calculate the amount of HBr in 100 c.c., and in 100 grams of the solution. (H = 1, Br = 80, Ag = 108.)

(London Inter. Pass, Extl., 1904.)

7. 0·200 gram of iron pyrites yields 0·700 gram of barium sulphate. What percentage of sulphur does the pyrites contain? (Fe = 55·9, S = 32, O = 16, Ba = 137·4.)

(Laboratory Class, Manc.)

8. A sample of coal contained 1·87 per cent. nitrogen. The ammonia evolved on heating 100 tons of this coal gave 2 tons 11 cwt. of ammonium sulphate. What percentage of the nitrogen was evolved from the coal as ammonia?

9. 1·575 gram of a monobasic acid took 50 c.c. of a solution of NaOH containing 20 grams per litre for neutralization. What is the molecular weight of the acid? (Na = 23.)

(Inter., Manc., 1911.)

10. A diad metal forms several oxides; it was found that when 411 grams of an oxide (containing 9·34 per cent. of oxygen) were heated with nitric acid, that 397·2 grams of the nitrate had been formed whilst 143·4 grams of another oxide (containing 13·39 per cent. of oxygen) were left undissolved.

Calculate the formulæ of the oxides and the atomic weight of the metal, and write out the equation representing the reaction which took place. (N = 14, O = 16.)

(London Pre. Sci., Veterinary, 1906.)

11. In a mixture of FeO and Fe_2O_3, 0·1000 gram of $KMnO_4$ was required for oxidation [in acid solution], and the Fe_2O_3

(total iron by precipitation) weighed 0·8000 gram; what was the composition of the mixture? (K = 39, Mn = 55, Fe = 56).

(Laboratory Class, Manc.)

12. Marignac found that 5·000 grams of strontium chloride containing 6 molecules of water of crystallization gave 3·442 grams of strontium sulphate. Calculate the *equivalent* of strontium. (H = 1, O = 16, S = 32, Cl = 35·5.)

(London Inter. Pass, Extl., 1904.)

13. An organo-metallic compound containing only carbon, hydrogen, and the metal gave, on combustion, the following numbers: 0·267 gram of substance gave 0·176 gram CO_2 and 0·108 gram H_2O, and there remained behind 0·223 gram of the metallic oxide in the combustion apparatus. The metal forms colourless salts. Find the equivalent of the metal and deduce a probable atomic weight by help of the periodic arrangement of the elements. (B.Sc. Hons., Manc.)

14. Thallous chloride (TlCl) reacted with gold bromide ($AuBr_3$) so that—

(*a*) 0·232 gram of thallous chloride gave 0·128 gram of gold.

(*b*) 0·294 „ „ „ 0·162 „ „

Construct the equation for the reaction. (Tl = 204, Cl = 35·46, Au = 197·2.)

15. D. Borar found (*J.C.S.*, 1911, **99**, 1415) that 1·000 gram of mercury reduced 0·2452 gram of potassium dichromate in the presence of hydrochloric acid. The chromium was converted into chromic chloride. Construct the equation for the reaction.

16. From the following data calculate what percentage of the whole hydrochloric acid escapes from a chimney connected with salt cake plant in which 8 tons of 90 per cent. salt is decomposed in 24 hours:—

(*a*) Hydrochloric acid in chimney gas is $\frac{1}{8}$ grain per cubic foot.

(*b*) Velocity of chimney gas corrected to standard temperature and pressure is 15 feet per second.

(*c*) Diameter of chimney at the point of observation is 4 feet. (Hons. Manc., Techl. Chem., 1894.)

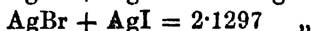
17. An analysis of a mixture of potassium chloride, bromide, and iodide is made by the following method:—

One gram of the mixed salts is precipitated by silver nitrate, and the total weight of silver chloride, bromide, and iodide is determined. Another gram is similarly precipitated and the chloride is converted into bromide by digestion with potassium bromide. A third gram is precipitated as before, and all the salts are converted into iodide by digestion with potassium iodide.

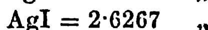
The weights obtained are as follows:—



$$AgCl + AgBr + AgI = 1{\cdot}7713 \text{ grams}$$



$$AgBr + AgI = 2{\cdot}1297 \text{ ,,}$$



$$AgI = 2{\cdot}6267 \text{ ,,}$$

Calculate the percentages of the potassium chloride, bromide, and iodide in the original mixture. (K = 39, Cl = 35·5, Br = 80, I = 127, Ag = 108.)

(Inst. Chem., Min., April, 1910.)

18. How would you soften a water having the following composition:—

	Grains per gallon.
Calcium carbonate ($CaCO_3$)	10
Calcium sulphate ($CaSO_4$)	15
Magnesium sulphate ($MgSO_4$)	5
Sodium sulphate (Na_2SO_4)	5
Sodium chloride ($NaCl$)	5

(Inst. Chem., Final, Mineral, 1911.)

When two or more chemical reactions take place in succession, it is not usually necessary to make a separate calculation for each reaction. In the determination of manganese dioxide in a specimen of pyrolusite the mineral is treated with hydrochloric acid, the chlorine evolved being passed into potassium iodide where iodine is liberated. The quantity of free iodine is found by determination of the quantity of sodium thiosulphate required to combine with it. The following reactions take place:—



$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$



$$2KI + Cl_2 = 2KCl + 2I$$



$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI$$

Inspection of these equations will show that 1 gram-molecule of manganese dioxide (86·93 grams) will correspond with 2 gram-molecules of sodium thiosulphate (2 × 158·14 = 316·28). So if 0·5621 gram of pyrolusite corresponded with 1·207 gram of anhydrous sodium thiosulphate, then the quantity of manganese dioxide present would be—

$$\frac{1{\cdot}207 \times 86{\cdot}93}{316{\cdot}28} = 0{\cdot}3317 \text{ gram}$$

or

$$\frac{0{\cdot}3317}{0{\cdot}5621} \times 100 = 59{\cdot}0 \text{ per cent.}$$

19. What weight of chlorine would be produced by the action of hydrochloric acid on 10·00 grams of manganese dioxide? What weight of iodine would this chlorine displace from a solution of potassium iodide? (Mn = 55, Cl = 35·5, I = 127.)

20. How much pyrolusite (82 per cent. manganese dioxide), and how much hydrochloric acid (33 per cent. hydrogen chloride) will be required to furnish the chlorine necessary to convert 40 grams of potassium hydroxide completely into chlorate and chloride?

21. Platinic chloride was added to a solution of ammonium chloride and the resulting precipitate, after ignition, left 1·700 grams of platinum. What weight of ammonium chloride was present in the solution? (Pt = 195, N = 14 H = 1, Cl = 35·5.) (Bd. of Ed., Stage II., 1910.)

22. 0·8876 gram of a sample of pyrolusite yielded 0·8027 gram of carbon dioxide when it was warmed with oxalic acid and dilute sulphuric acid. What percentage of MnO_2 did it contain? (Mn = 55.) (B.Sc., Manc.)

23. The gases from the action of heat on 1·103 gram of

lead nitrate [$Pb(NO_3)_2$] were passed into a solution of potassium iodide. What weight of iodine would be liberated? (Pb = 207, N = 14, O = 16, K = 39, I = 127.) (B.Sc., Manc., 1911.)

[*Note.*—The student will find it an instructive exercise to test the result of his calculation experimentally.]

24. If 1·04 gram of silicon fluoride were entirely decomposed by water in a platinum dish, and the precipitate formed were collected and ignited, what would its weight be?

(B.Sc., Manc.)

25. Calculate the weight of quicklime required to neutralize the hardness of 1,000,000 gallons of water containing 10 grains of calcium carbonate (dissolved as bicarbonate) per gallon.

Certain Indirect Analyses.—The following example illustrates a common case of indirect analysis. 0·9031 gram of mixed sodium and potassium chlorides was treated with sulphuric acid, and the resulting mixture of sulphates weighed 1·0784 gram. What were the amounts of the two chlorides in the original mixture?

The equations involved are—



$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

whence 116·92 grams of sodium chloride give 142·07 grams of sodium sulphate.



$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$

whence 149·12 grams of potassium chloride give 174·27 grams of potassium sulphate.

If x and $0·9031 - x$ represent the quantities of sodium and potassium chloride respectively—

The x gram of sodium chloride give $\frac{142·07x}{116·92}$ gram of sulphate.

$(0·9031 - x)$ gram of potassium chloride give

$$\frac{174·27\ (0·9031 - x)}{149·12} \text{ gram of sulphate}$$

and the weight of the mixed sulphates is

$$\frac{142\cdot07x}{116\cdot92} + \frac{174\cdot27}{149\cdot12}(0\cdot9031 - x) = 1\cdot0784$$

Solving for x we get—

$$x\left(\frac{142\cdot07}{116\cdot92} - \frac{174\cdot27}{149\cdot12}\right) = 1\cdot0784 - 0\cdot9031 \times \frac{174\cdot27}{149\cdot12}$$

$$x(1\cdot2151 - 1\cdot1687) = 1\cdot0784 - 1\cdot0555$$

$$x = 0\cdot494$$

i.e. sodium chloride = 0·494 gram.
and potassium chloride = 0·409 „

The student is advised to apply some of the considerations in Chapter I to this problem. For instance, if the experimental error in the weight of the mixed sulphates may be 0·2 mgr., what error would that produce in the result calculated? [6 mgr.]

Example No. 30 (below) is a case where a small error in weighing will produce a large error in the result calculated—so large that the method of experiment would in that case not be used by a good analyst.

26. A quantity of a mixture of potassium iodide and sodium chloride transformed into the normal sulphates is found to weigh the same as the original salts; determine the composition of the mixture. (K = 39, Na = 23, Cl = 35·4, I = 126·5, S = 32, O = 16.) (Laboratory Class, Manc.)

27. A mixture of potassium chloride and iodide is converted into potassium sulphate, and the weight of the sulphate is found to be the same as that of the original mixture. In what proportions were the salts present in the mixture? (K = 39·1, Cl = 35·4, I = 126·9, S = 32, O = 16.)
(Laboratory Paper, Manc.)

28. A mixture of dry calcium sulphate and calcium carbonate, when strongly heated over the blowpipe, is reduced to 75·0 per cent. of its original weight. What are the proportions of the two compounds in the mixture? (Ca = 40, S = 32, C = 12.) (Inter. B.Sc., Leeds.)

29. 2·000 grams of a mixture of sodium and potassium chlorides gave 4·300 grams of silver chloride. What was the percentage of each salt in the mixture?

30. A mixture of barium monoxide and barium peroxide contained 88·0 per cent. of barium. What was the percentage composition of the mixture? What would be the error in the calculated percentages if there were an error of (*a*) 1, (*b*) 0·1, in the percentage of barium?

The Volume-Weight Relationships of Gases.—So far, only the weights of the substances taking part in a chemical reaction have been calculated. If any reagent is gaseous, its volume is deduced from its weight, or *vice versâ*, by use of the principle laid down in Chapter IV.

If, for instance, in the example referring to zinc and sulphuric acid (p. 54), it were required to find the volume of moist hydrogen produced at 15° C. and 750 mm., then—



$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

98·086 grams hydrogen sulphate give 2·016 grams or 22·4 litres of hydrogen at N.T.P. (see p. 31).

$\therefore$ 700 grams hydrogen sulphate give $22{\cdot}4 \times \frac{700}{98{\cdot}086}$ litres of hydrogen at N.T.P.

or $$22{\cdot}4 \times \frac{700}{98{\cdot}086} \times \frac{288}{273} \times \frac{760}{737{\cdot}3} = 174 \text{ litres moist}$$

at 15° and 750 mm.

The datum used for transforming weights into volumes, and *vice versâ*, is either of the following, and practice in their use will soon show which is the more convenient for any given case.

I. The gram-molecular weight of any gas at N.T.P. occupies 22·4 litres (approximate, but used in all except the most accurate work. See p. 31).

II. One litre of hydrogen at N.T.P. weighs almost exactly 0·09 gram. Hence one litre of any gas at N.T.P. weighs $0{\cdot}09 \times d$ grams, where d is the density of the particular gas referred to hydrogen as unity.

Now d is approximately $= \dfrac{\text{molecular weight}}{2{\cdot}016}$

or less exactly $= \dfrac{\text{molecular weight}}{2}$

The approximation $d = \dfrac{\text{molecular weight}}{2}$ is often sufficiently accurate, but gives results differing by 0·8 per cent. from those obtained by use of datum I. (above).

The answers given for the following exercises are calculated from the data :—

The gram-molecular weight of a gas occupies 22·4 litres at N.T.P., or

One litre of a gas weighs $0{\cdot}09 \times \dfrac{\text{molecular weight}}{2{\cdot}016}$ gram at N.T.P.

Since these data bear small inaccuracies, exact atomic weights give as a rule results of only the same degree of accuracy as approximate atomic weights. These latter are therefore used, with the exception of H = 1·008, which differs by 0·8 per cent. from H = 1·000.

The following approximate atomic weights are accurate to 1 in 1000 :—

Barium ...	137·4	Manganese ...	55
Calcium ...	40·1	Mercury ...	200·6
*Carbon ...	12	*Nitrogen ...	14
*Chlorine ...	35·5	*Oxygen ...	16
Copper ...	63·6	Potassium ...	39·1
*Hydrogen ...	1·008	*Silver ...	108
*Iron ...	55·8	*Sodium ...	23
Lead ...	207	*Sulphur ...	32·1
Magnesium	24·3	Zinc ...	65·4

31. What is the weight of 220 c.c. of each of the following gases, measured at 0° C. and 760 mm.: (*a*) hydrogen, (*b*) carbon dioxide, (*c*) nitric oxide, (*d*) nitrous oxide?

32. What is the volume occupied at 0° C. and 760 mm. pressure by 1·00 gram of each of the following gases: (*a*) hydrogen, (*b*) carbon dioxide, (*c*) nitric oxide, (*d*) nitrous oxide?

33. Calculate the volume (at normal temperature and pressure) of oxygen obtainable by heating in a test tube 1·00 gram of each of the following substances: Potassium chlorate, red lead, potassium nitrate.

34. What weight of water will be produced by passing 10 litres of hydrogen measured at 760 mm. and 0° C. over a 1·000 gram of heated copper oxide? (Inter. B.Sc., Leeds.)

35. What weight of oxygen could be obtained from 54 grams of mercuric oxide? What volume would this weight of oxygen occupy at −91° C. and 7 atmospheres pressure? (Hg = 200, O = 16.) (1st Dipl. Dental Surgery, Manc.)

36. If 15·0 grams of water are decomposed into the constituent gases, what volume will these gases occupy at N.T.P.? (Bd. of Ed., Stage I., Inorg., 1909.)

37. What weight of zinc will be dissolved by 250 grams

* Approximate atomic weights starred should be remembered by the student; the others are invariably (and the starred ones often) appended to an examination question when necessary.

of dilute sulphuric acid containing 20 per cent. of H_2SO_4, and what volume of gas measured at N.T.P. will be evolved?

(Bd. of Ed., Stage I., Inorg., 1907.)

38. Give equations representing the formation of hydrogen by the action of (*a*) steam, and (*b*) dilute sulphuric acid on iron. What weight of iron would be necessary in each case for the preparation of 300 litres of hydrogen measured at 27° C. and 740 mm. pressure? (General Class, Manc.)

39. What volume of oxygen, measured at 15° C. and 760 mm., can be obtained by the complete decomposition of [the hydrogen peroxide in] 20 c.c. of an aqueous solution containing 30 grams of hydrogen peroxide per litre?

(1st "Conjoint," March, 1910.)

40. An acidified solution of hydrogen peroxide, on treatment with excess of potassium permanganate, gave 32·6 times its volume of oxygen. What volume of oxygen, measured at N.T.P., would it evolve (*a*) if heated alone, (*b*) if some finely divided manganese dioxide were introduced, (*c*) if it were neutralized by means of dilute alkali, and then finely divided manganese dioxide introduced?

41. Calculate the volume of nitrous oxide, measured at N.T.P., obtainable from 20 grams of ammonium nitrate, and the volume of nitrogen it would contain.

(Bd. of Ed., Stage I., Inorg., 1910.)

42. One gram of phosphorus was placed in a litre globe of air which was sealed up at N.T.P. The phosphorus was ignited by gently warming the globe. What was the final pressure in the globe when it had cooled to 13° C.? (The percentage of oxygen in air by volume = 20·9.)

(General Class, Manc.)

43. A piece of sodium was completely converted into chloride by the absorption of 250 c.c. of chlorine (measured at 10° and 720 mm.). What was the weight of the sodium used and of the chloride formed?

(Bd. of Ed., Stage II., Inorg., 1907.)

44. What weight of common salt would be required to furnish sufficient hydrogen chloride to neutralize 100 grams

of a 30 per cent. solution of caustic soda? What would be the volume of the gas at normal temperature and pressure?

(Bd. of Ed., Stage I., Inorg., 1906.)

45. What weight of carbon dioxide could be made by burning 100 grams of carbon, and what volume would this gas occupy at 546° C. and 112 mm. pressure?

(General Class, Manc.)

46. 10 grams of carbon are strongly heated in a current of steam. Assuming that the reaction takes place quantitatively with the formation of carbon monoxide and hydrogen, calculate the volume of each gas produced, and express in litres at N.T.P.

(Manc. Sch. of Tech., 1st Year Course, 1910.)

47. What volume of carbonic acid gas can be formed by the action of hydrochloric acid on 100 grams of the following: acid potassium carbonate, calcium carbonate, normal bismuth carbonate? ($K = 39$, $Ca = 40$, $Bi = 210$.)

(General Class, Manc.)

48. How much sulphuric acid will be required to decompose 50 grams of anhydrous potassium carbonate, and what volume of carbon dioxide measured at 12° and 740 mm. will be obtained? (Dauntsey Entrance Med. Sch., Manc.)

49. If 11 grains of $BaSO_4$ are obtained from the sulphur present in 5 cubic feet of coal gas, express the result in terms of number of grains of sulphur per 100 cubic feet of gas, and in milligrams of sulphur per litre, and as c.c. of H_2S per litre.

50. What weight of sulphur would be sufficient to convert all the oxygen in the air of a room 4 metres high, 6 metres long, and 5 metres wide into sulphur dioxide? The air of the room is to be taken at 20° C. and 760 mm. pressure. [Assume air to contain 21 per cent. of oxygen, by volume.]

(1st "Conjoint," Mar., 1909, adapted.)

51. It was found that 224 c.c. of sulphur dioxide at N.T.P. just decolourised 100 c.c. of a solution of potassium permanganate in dilute sulphuric acid. Calculate the strength of the potassium permanganate solution in grams per litre.

(Inter., Manc., 1911.)

52. In order to determine the strength of dilute sulphuric acid having the density 1·091, 2 grams of pure magnesite ($MgCO_3$) were treated with 10 c.c. of the acid. After all action had ceased it was found that 0·8743 gram of magnesite remained undissolved. Calculate the number of grams of H_2SO_4 in (*a*) a litre, (*b*) a kilogram, of the dilute acid.

What volume of carbon dioxide at 13° C. and 740 mm. pressure would be produced in the above reaction?

(London Inter., Veterinary, 1907.)

53. Exactly 3 grams of magnesite ($MgCO_3$) were added to 5·000 grams of dilute sulphuric acid; after all action had ceased, it was found that 0·480 gram was left undissolved; calculate the percentage strength of the sulphuric acid.

In this reaction what volume of carbon dioxide would be evolved, measured at (*a*) 0° C. and 760 mm., (*b*) 13° C. and 741 mm.? (London Pre. Sc., Vet., 1905.)

54. 8·000 grams of sulphur are burnt in oxygen: what is the volume of the resulting gas under normal conditions, and what volume would the gas occupy at 91° C. and 380 mm. pressure? (S = 32.) (General Class, Manc.)

55. What weight of hydrogen sulphide and of sulphur dioxide could be formed from 10·00 grams of sulphur, and what volume would these gases occupy under standard conditions? (S = 32.) (General Class, Manc.)

56. Calculate the volume of sulphur dioxide, measured at normal temperature and pressure, which the solution of 100 grams of copper in excess of concentrated sulphuric acid should give according to the usual equation. Why would the actual yield be less than this?

(Manc. Sch. of Tech., 1st Year, 1911.)

57. What is the usual equation representing the action of strong sulphuric acid on metallic copper? What volume of gas ought to be obtained by the solution of 76·2 grams of copper, the gas being measured at 21° C. and 791 mm.?

(London Inter. Pass, Extl., 1905.)

58. 0·0239 gram of carbon was treated with hydrogen at

1150°. (Bone and Coward, *J.C.S.*, 1910, **97**, 1224.) In the products of the reaction 42·43 c.c. of methane at 0° and 760 mm. were found. What percentage yield is this, reckoned upon the carbon used?

59. 100 c.c. of a gas were completely decomposed by heated tin. The tin was converted into stannous sulphide with an increase in weight of 0·144 gram. The residual gas consisted of hydrogen, and when passed over heated copper oxide gave 0·081 gram of water. Show how the formula of the gas may be deduced from these data, given that a litre of hydrogen at N.T.P. weighs 0·09 gram. (Inter., Manc., 1910.)

60. Calculate by the shortest method you know the volume of gas which would be evolved by dissolving in hydrochloric acid 10·0 grams of a mixture of 8·4 parts by weight of magnesium carbonate with 10·0 parts of calcium carbonate. Find also the weight of silver nitrate required to precipitate completely the chloride formed. (Ca = 40, Mg = 24, Ag = 108.) (Inter., B.Sc., Manc.)

61. 1·000 gram of a mixture of the carbonates of calcium and magnesium gave 240 c.c. of carbon dioxide (N.T.P.) Calculate the composition of the mixture. (B.Sc., Manc.)

62. What is the ratio of the volumes of hydrogen and carbon dioxide (both measured at 770 mm. and 15° C.) evolved respectively by the interaction of (*a*) 60 c.c. of 30 per cent. hydrochloric acid on an excess of zinc, (*b*) 40 c.c. of 30 per cent. hydrochloric acid on an excess of boiling sodium carbonate solution? (Inter., B.Sc., Leeds.)

63. A liquid petroleum of specific gravity 0·7803 is found to contain 85·0 per cent. of carbon and 15·0 per cent. of hydrogen. What is the minimum volume of air necessary for the complete combustion of 10·0 litres of it, and what weight of water and volume of carbon dioxide will be formed? Air may be assumed to contain 21·0 per cent. of oxygen, and the measurements to be made at N.T.P.

(Inter., B.Sc., Leeds.)

64. A fuel used in a gas producer contains 12 per cent. of ash and 72 per cent. of carbon. The ashes made contain 5 per cent. of unburnt carbon; the gas produced contains 0·165 of an ounce of carbon per cubic foot of gas at 0° C. and 760 mm. pressure. What volume of gas, measured under these conditions, is being produced per ton (2240 lbs.) of fuel used? (Hons., Manc., Fuel, 1909.)

CHAPTER VIII

THE REACTING VOLUMES OF GASES—GAS ANALYSIS

THE equation



$$2CO + O_2 = 2CO_2$$

indicates that two molecules of carbon monoxide react with one molecule of oxygen to produce two molecules of carbon dioxide. Hence $2n$ molecules of carbon monoxide react with n molecules of oxygen to produce $2n$ molecules of carbon dioxide. These $2n$ molecules of carbon monoxide will occupy twice the volume of n molecules of oxygen and the same volume as the $2n$ molecules of carbon dioxide, always assuming that the three gases are measured under the same conditions of temperature and pressure (Avogadro's hypothesis). Thus a direct inspection of the equation enables the statement to be made that 2 volumes of carbon monoxide react with 1 volume of oxygen to produce 2 volumes of carbon dioxide. By simple proportion the reacting quantities can be calculated for any given amount of any one reagent. Thus—

(A) 150 volumes of carbon monoxide will, on complete combustion, combine with 75 volumes of oxygen, and produce 150 volumes of carbon dioxide, the three measurements being all made at the same temperature and pressure.

(B) A mixture of 50 volumes of carbon monoxide and 50 volumes of oxygen evidently contains an excess of oxygen beyond that required for complete combustion of the carbon monoxide. If, then, the mixture be inflamed,

the 50 volumes of carbon monoxide will unite with 25 volumes of oxygen, producing 50 volumes of carbon dioxide; with this will be mixed the 25 volumes of oxygen in excess of that required for complete combustion.

The application of corrections for change in temperature and pressure when these are not constant may be made by the use of the principles explained in Chapter III.

1. 100 c.c. of carbon monoxide are mixed with 40 c.c. of oxygen and exploded. If the resulting mixture is shaken with caustic potash, what volume of gas will remain, and what gas will it be? (Bd. of Ed., Stage I., Inorg., 1907.)

2. If 10·0 litres of carbon monoxide at 0° and 760 mm. are burned, what volume of oxygen at the same temperature and pressure will be consumed, and what will be the volume of carbon dioxide formed if measured at 15° and 740 mm.? (Bd. of Ed., Stage II., Inorg, 1905.)

3. What volume of oxygen at N.T.P. is required for the combustion of 56 grams of carbon monoxide. (Inter. B.Sc., Manc.)

4. How many litres of oxygen, measured at 20° and 750 mm., are necessary for the complete combustion of 150 grams of marsh gas? (Bd. of Ed., Stage II., 1909.)

5. What change in volume would take place in one litre of oxygen by—

(*a*) burning sulphur in it,
(*b*) converting 6 per cent. of it into ozone,
(*c*) combining it with twice its volume of carbon monoxide? (London Inter., Intl., 1908.)

6. How many litres of hydrogen, measured at 20° and 750 mm., are necessary to combine with the oxygen evolved by the complete decomposition of 50·0 grams of potassium chlorate? (Dauntsey Entrance Medical Schol., Manc.).

7. How many grams of 10 per cent. hydrogen peroxide would be required to oxidize 12 grams of lead sulphide? If the volume of oxygen obtained by heating this quantity of

hydrogen peroxide were combined with carbon monoxide, what would be the volume of the resulting gas measured at 15° and 750 mm.? (London Inter. Veterinary, 1907.)

8. A sample of gas had the following percentage composition: hydrogen, 45; marsh gas, 30; carbon monoxide, 20; acetylene 5. 100 volumes of it were mixed with 160 volumes of oxygen and the mixture exploded. Calculate the volume and the composition of the resulting mixture of gases (all being supposed dry). (London Inter. Extl., 1906.)

9. Calculate the volume and composition of the gases which would result from exploding a mixture of 150 volumes of oxygen and 100 volumes of gas having the percentage composition: hydrogen, 46; marsh gas, 28; carbon monoxide, 18; ethylene, 6; carbon dioxide, 2.

(London Inter. Veterinary, 1907.)

10. Coal gas of the composition given below is burnt in air:—

	Per cent.
Hydrogen (H_2)	48·0
Methane (CH_4)	26·0
Ethane (C_2H_6)	2·0
Ethylene (C_2H_4)	3·0
Benzene (C_6H_6)	1·0
Carbon monoxide (CO)	15·0
Carbon dioxide (CO_2)	2·0
Carbon disulphide (CS_2)	0·1
Nitrogen (N_2)	2·9
	100·0

Name the products and give the quantities of each produced per litre at N.T.P. of gas burnt, stating your results in c.c. measured at 100° C. and 760 mm.

(Inst. Chem. Inter., Jan., 1911.)

11. The density of liquid carbon dioxide was found to be 0·88 compared with water at 4° C. What volume of gas at N.T.P. would be formed by the evaporation of 100 c.c. of the liquid, and what volume of carbon monoxide measured at

27° and 720 mm. would be formed by passing this gas over heated carbon? (C = 12, O = 16.)

(General Class, Manc.)

12. If 100 c.c. of hydrogen and 100 c.c. oxygen, both at 27° C. and 216 mm., be mixed and fired, at what temperatures would the products of their ignition occupy 300 c.c. at 216 mm.

13. Calculate the number of volumes of hydrogen (to four decimal places) which combine with one volume of oxygen when 6870·1 volumes of hydrogen, mixed with 3139·7 volumes of oxygen and exploded, left 9·2 volumes of oxygen uncombined. (London Inter. Pass, Extl., 1905.)

14. If the density of oxygen is 15·90 and the atomic weight of oxygen 15·86 [H = 1] what are the combining volumes of oxygen and hydrogen and what is the density of electrolytic gas? (Hons. B.Sc., Manc.)

Determination of the Formula of a Pure Gas.—An example of the determination of the formula of a gas is found in the reaction between chlorine and excess of ammonia solution (see text-book for practical details). The experiment shows that 3 volumes of chlorine displace from an unknown volume of ammonia, 1 volume of nitrogen. Now, chlorine and hydrogen unite only in one ratio, namely, in equal volumes. Hence the unknown volume of ammonia gas would yield on decomposition nitrogen and hydrogen in the ratio of—

$$\frac{\text{1 volume nitrogen}}{\text{3 volumes hydrogen}}$$

$$i.e = \frac{\text{1 molecule nitrogen}}{\text{3 molecules hydrogen}} \text{ (by Avogadro's hypothesis)}$$

$$= \frac{\text{1 atom nitrogen}}{\text{3 atoms hydrogen}}$$

i.e. ammonia is NH_3 or N_2H_6, or some other simple multiple of NH_3. The formula is finally proved to be NH_3 by a determination of the density of the gas

15. A mixture of chlorine with an oxide of chlorine gave on explosion an expansion from 100 c.c. to 130 c.c. The exploded gas was found to contain 70 c.c. of chlorine and 60 c.c. of oxygen. What was the oxide, and how much of it was there in the mixture? (1st Year Hons., Manc.)

16. 12 c.c. of gaseous ammonia were completely burnt when fired with 18 c.c of an oxide of nitrogen, and 15 c.c. of nitrogen remained in the eudiometer after the condensation of the steam. What is the formula of the oxide of nitrogen?

(1st Year Hons., Manc.)

17. A gaseous compound of carbon and hydrogen gave the following results on combustion.

Volume of gas	14·8 c.c.
Volume of gas and excess of air ...	200·2 c.c.
Volume after explosion	178·0 c.c.
Volume after removal of carbon dioxide	148·4 c.c.

What was its molecular formula?

18. Find the molecular formula of a gaseous oxide of carbon from the following data referring to the combustion of the substance with an excess of oxygen and consequent production of carbon dioxide. (Diels and Wolf, *Ber.*, 1906, **39**, 689.)

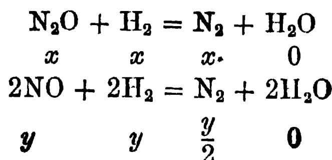
Volume of gas	9·86 c.c.
Volume of gas and excess of oxygen ...	104·5 c.c.
Volume after explosion	104·1 c.c.
Volume after treatment with potassium hydroxide	74·8 c.c.

When dealing with a gaseous mixture whose constituents are known, the relative amounts of the latter may be determined by gas-volumetric processes.

EXAMPLE.—When 100 c.c. of a mixture of nitrous and nitric oxides were mixed with 200 c.c. of hydrogen and fired in a eudiometer, 80 c.c. of nitrogen remained. What was the composition of the mixture? (Inter. B.Sc., Manc.)

The two equations are written for the combustion of the two oxides separately. Note that there is sufficient

hydrogen to decompose completely either oxide if present alone; therefore also to decompose any mixture of the two. Underneath each member of the equation is placed an expression showing the volume of it reacting with or resulting from x c.c. of nitrous oxide or y c.c. of nitric oxide as follows :—



$$\begin{array}{cccc} N_2O & + \; H_2 & = \; N_2 & + \; H_2O \\ x & x & x & 0 \end{array}$$

$$\begin{array}{cccc} 2NO & + \; 2H_2 & = \; N_2 & + \; 2H_2O \\ y & y & \frac{y}{2} & 0 \end{array}$$

Then $x + y = 100$

and $x + \frac{y}{2} = 80$

whence $x = 60$ c.c. of nitrous oxide
$y = 40$ c.c. of nitric oxide

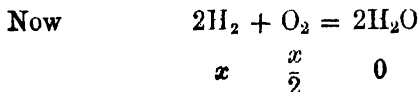
A similar calculation to the above is made in the analysis of mixtures of methane, hydrogen, and nitrogen by explosion with a measured excess of oxygen. After cooling to the original temperature the contraction is noted. The carbon dioxide is then absorbed by a solution of potassium hydroxide, and its amount thus found. Corrections for changes in temperature and pressure and for the presence of varying amounts of water vapour were formerly required in analyses of this kind, but at the present time the best forms of apparatus are arranged to keep a constant temperature throughout the analysis, and the measurement is either that of volume at constant pressure or, what is almost the same, pressure at constant volume. Unless all the measurements are those of dry gases (an operation of some difficulty), it is usual to keep the walls of the measuring tube moist with water or dilute sulphuric acid. In this way, since the temperature does not vary, a constant pressure of aqueous vapour is ensured for all the

measurements. If these are volumes at, say, 14° C. and 760 mm., then the same readings would represent quantities of dry gas at 14° and 748 mm., *i.e.* at a constant temperature and pressure. (The vapour pressure of water or dilute sulphuric acid at 14° is approximately 12 mm.) If the measurements are pressures at, say, 14° C. and at constant volume, the apparatus is so constructed that the readings express the difference in pressure between the moist gas and saturated aqueous vapour at the same temperature contained in the other limb of a U-tube manometer. This difference is obviously the partial pressure of the dry gas, so that the effect of the water vapour is automatically eliminated.

To return to the calculation of the analysis, the example may be taken—

Gas (hydrogen + methane + nitrogen) ...	83·9	volumes
Gas + oxygen	484·5	„
Mixture after explosion	349·9	„
Mixture after treatment with KOH ...	322·1	„
Here the contraction = 484·5 − 349·9 =	134·6	„
And the carbon dioxide = 349·9 − 322·1 =	27·8	„

Let there be x volumes of hydrogen and y volumes of methane in the original 83·9 volumes of gas.

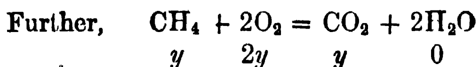


Now $2H_2 + O_2 = 2H_2O$

$$x \qquad \frac{x}{2} \qquad 0$$

The water produced has no effect on the volume measurement.

Since x volumes of hydrogen and $\frac{x}{2}$ volumes of oxygen disappear from the gas, the presence of x volumes of hydrogen accounts for a contraction on explosion of $\frac{3x}{2}$ volumes.



Further, $CH_4 + 2O_2 = CO_2 + 2H_2O$

$$\begin{matrix} y & 2y & y & 0 \end{matrix}$$

Since y volumes of methane and $2y$ volumes of oxygen disappear from the gas, and are replaced by y volumes of carbon dioxide, the presence of y volumes of methane accounts for a contraction of $2y$ volumes and for the formation of y volumes of carbon dioxide. The nitrogen is unaffected.

Then contraction due to combustion of hydrogen $= \frac{3x}{2}$

And contraction due to combustion of methane $= 2y$

Total contraction $= \frac{3x}{2} + 2y = 134.6$

Also, total carbon dioxide $= y = 27.8$

whence x, hydrogen $= 52.7 = 62.8$ per cent.

y, methane $= 27.8 = 33.1$ „

and $83.9 - (x + y)$, nitrogen $= 3.4 = 4.1$ „

Note that the nitrogen is determined by difference, so that such an analysis will of necessity give results adding up to 100 per cent.

19. If 100 volumes of air are mixed with 80 volumes of hydrogen and an electric spark is passed through the mixture, what will be the volume and composition of the remaining gas measured at the same temperature and pressure?

(Bd. of Ed., Stage I., Inorg., 1910.)

20. To 100 c.c. of a mixture of oxygen and nitrogen, standing over water, 100 c.c. of hydrogen were added, and the mixture was fired. After cooling the residual gases (nitrogen and hydrogen) occupied 92 c.c. What was the composition of the mixture? (General Class, Manc.)

21. 100 c.c. of a mixture of carbonic oxide and marsh gas were added to 200 c.c. of oxygen in a eudiometer. After firing

and cooling the residual gas measured 235 c.c. Calculate the composition of the mixture. (1st Year Hons. Class, Manc.)

22. 100 volumes of a mixture of oxygen, nitrous oxide and nitrogen were mixed with 150 of hydrogen, and exploded. On cooling, 90 volumes were left. To these 50 volumes of oxygen were added, and the mixture was exploded. The residue on cooling measured 95 volumes. What was the composition of the mixture? (Dauntsey Entrance Med. Schol., Manc.)

23. A mixture of nitrous and nitric oxides with nitrogen was analysed as follows. All readings were taken under the same conditions of temperature and pressure over water.

Volume of mixture	17·0 c.c.
Volume of mixture and excess of hydrogen	36·1 „
Volume of mixture after reaction and cooling	17·0 „

The excess of hydrogen was then determined by explosion with oxygen.

Volume after adding oxygen to residue ...	25·5 c.c.
Volume after exploding	19·2 „

What is the percentage composition of the mixture?

24. 100 volumes of a mixture of carbonic oxide and acetylene were mixed with 250 volumes of oxygen in a eudiometer and fired. After cooling the residual gases occupied 260 volumes, and after treatment with potash the residual oxygen occupied 120 volumes. What was the composition of the mixture? (1st Year Hons., Manc.)

25. 100 c.c. of a mixture of carbon disulphide vapour and cyanogen were mixed with 300 c.c. of oxygen and fired. The contraction on cooling was 30 c.c., the SO_2 formed was 60 c.c., the CO_2 formed was 170 c.c. What was the composition of the mixture? (1st Year Hons., Manc.)

26. To a mixture of acetylene, hydrogen, and carbon monoxide, occupying 20 c.c. (corrected), 50 c.c. of oxygen were added and a spark passed. After cooling, the residual gases

contained 16 c.c. of carbon dioxide and 36 c.c. of unburnt oxygen. What was the composition of the mixture?

(Hons., Manc., 1911.)

27. 40 c.c. of a mixture of hydrogen, methane, and nitrogen were exploded with 10 c.c. of oxygen. After cooling, the residual gas measured 36·5 c.c. On treatment with caustic potash the volume diminished to 33·5 c.c., and on treatment with alkaline pyrogallol to 32 c.c. Calculate the percentage composition of the original mixture. (B.Sc., Manc., 1910.)

28. Given a gaseous mixture of nitrogen, oxygen, carbon monoxide, and acetylene, how would you prove the presence of each of the gaseous constituents? If 0·027 gram of water was produced after explosion of 150 c.c. of the mixture with oxygen, what was the percentage of acetylene in the original mixture? (B.Sc., Manc., 1911.)

29. A mixture of carbon monoxide, hydrogen, ethylene and nitrogen was analysed with the following results:—

Volume of gas	102·5
After treatment with bromine	89·55
After treatment with ammoniacal cuprous chloride	46·6
After admixture with oxygen and air	411·1
After explosion	344·0

Calculate the percentage composition.

30. 352·0 volumes of a coal mine gas, after treatment with caustic potash, become 351·0 volumes; after explosion with a small amount of electrolytic gas ($2H_2 + O_2$), 342·8 volumes; after treatment of this with caustic potash, 338·5 volumes. Calculate the percentages of carbon dioxide and of methane, assuming that the only hydrocarbon present is methane.

31. A sample of gas known to contain carbon dioxide, carbon monoxide, ethylene, methane, hydrogen, and nitrogen, was analysed as follows: 86·0 volumes on treatment with caustic potash were reduced to 84·9 volumes; on further treatment with Nordhausen acid and caustic potash the volume was reduced to 82·6. This residual gas was thereupon exploded with 55·77 volumes of oxygen and 326·21 volumes of

air (free from carbon dioxide). The volume after explosion was 383·88; after treatment with caustic potash it was reduced to 340·62. Assuming that the original gas contained 2·3 per cent. of nitrogen, calculate its composition from the foregoing analysis. (Fuel, Manc., 1902.)

32. 163 volumes of a sample of coal gas were reduced to 161·8 volumes over caustic potash, and afterwards to 155 volumes over fuming sulphuric acid. 95 volumes of the residual gas were exploded in a eudiometer with 600 volumes of oxygen. After the gas had cooled it measured 539·5 volumes, and on treatment with caustic potash was further reduced to 492·5 volumes. Assuming that the gas contains no nitrogen, and that the only saturated hydrocarbon present is methane, calculate its composition from the foregoing figures.

(Fuel Class, Manc., 1901.)

33. Calculate from the following data, the composition of a mixture of methane, ethane, and nitrogen :—

Volume of gas taken	53·5 c.c.
Volume of oxygen added	452·0 „
Volume after explosion	405·8 „
Volume after treatment with KOH ...	349·2 „

(London Hons. Intl., 1908.)

34. A mixture of carbonic oxide, methane, and ethane, measuring 10 c.c. was mixed with 40 c.c. of oxygen and fired in a moist eudiometer. After cooling, the residual gases were found to consist of 12 c.c. of carbonic acid and 23 c.c. of unconsumed oxygen. What was the composition of the mixture? (B.Sc. Hons., Manc.)

35. 60 c.c. of a mixture of carbon disulphide and carbon monoxide were mixed with 240 c.c. of oxygen in a eudiometer and fired; after cooling, the residual gases, CO_2, SO_2, and O_2 occupied 238 c.c., of which 132 c.c. were absorbed by potash. What was the composition of the mixture, and what percentage of the CS_2 was burnt to SO_3? (B.Sc. Hons., Manc.)

36. 1 litre of hydrogen containing small amounts of methane and of nitrogen was treated with palladium, which

removed all but 38·8 c.c. of gas. 99·6 volumes of this was mixed with air and oxygen to a total volume of 566·5 and exploded. Its volume then was 413·2, and after treatment with potash, 402·1. Find the percentages of nitrogen and of methane in the original gas.

37. A sample of gas containing carbon monoxide, carbon dioxide, nitrous oxide, and nitrogen was analysed with the following results:—

Volume of gas used	148·9
Volume after treatment with moist potash ...	52·6
After addition of hydrogen	275·6
After addition of electrolytic gas ($2H_2 + O_2$) ...	310·4
After explosion *	245·1
After treatment with ammoniacal Cu_2Cl_2 ...	235·7

Calculate the percentage composition.

38. A mixture of oxygen and carbon monoxide is exposed to the action of ultraviolet light. Ozone and carbon dioxide are the new gases formed in the reaction. If 100·00 c.c. of gas were taken in which the ratio $\frac{O_2}{CO}$ was 1·015, how many c.c. of each of the gases will be found in the residue which measures 85·87 c.c. and has the ratio $\frac{CO_2}{CO} = 0{\cdot}2419$?

(Chapman, Chadwick, and Ramsbottom, *J.C.S.*, 1907, 944.)

39. It is proposed to analyze mixtures which contain (*a*) methane, carbon monoxide, hydrogen, and nitrogen; (*b*) methane, ethane, hydrogen, and nitrogen, by combustion with excess of oxygen and measurement of (i.) volume of gaseous mixture, (ii.) volume of oxygen added, (iii.) contraction after explosion, (iv.) volume of carbon dioxide produced, (v.) residual oxygen. Show in each case whether it is possible to calculate the composition of the original mixture or not.

Would it be possible to analyse these two mixtures by passing measured volumes of each over red-hot copper oxide and weighing separately the water and carbon dioxide produced?

* A negligible amount of CO_2 was formed.

CHAPTER IX

VOLUMETRIC ANALYSIS (SOLUTIONS)

THE principles and methods of volumetric analysis can only be studied in the laboratory. The following sections, therefore, contain only an outline of the nomenclature, and illustrations of the methods which should be used in calculation.

Normal Solutions of Acid and Alkali.—A normal solution of an acid contains 1 gram-equivalent (*i.e.* 1·008 gram) of hydrogen replaceable by a metal, per litre. For example, normal hydrochloric acid contains (1·008 + 35·46) grams of HCl per litre. Normal sulphuric acid contains ½(2·016 + 32·07 + 64·00) grams of H_2SO_4 per litre, because the gram-molecular weight of sulphuric acid (2·016 + 32·07 + 64·00 grams) contains 2 gram-atoms of hydrogen.

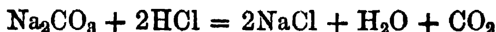
A normal solution of an alkali is exactly equivalent to a normal solution of an acid. For example, since


$$\underbrace{\underset{23\cdot00 + 16\cdot00 + 1\cdot008}{NaOH}}_{40\cdot01} + \underbrace{\underset{1\cdot008 + 35\cdot46}{HCl}}_{36\cdot47} = NaCl + H_2O$$

then normal caustic soda solution contains 40·01 grams of NaOH per litre, or 23·00 grams, *i.e.* the equivalent, of Na. Normal baryta solution contains ½(137·37 + 32·00 + 2·016) grams of $Ba(OH)_2$, because 1 gram-molecule of $Ba(OH)_2$ is equivalent to 2 gram-molecules of HCl—


$$Ba(OH)_2 + 2HCl = BaCl_2 + 2H_2O$$

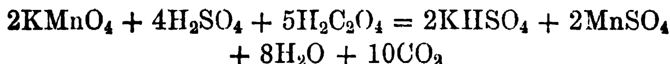
In certain reactions salts of weak acids (*e.g.* sodium carbonate, Na_2CO_3, and borax, $Na_2B_4O_7$) behave as alkalies, and neutralize stronger acids, *e.g.*—



$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

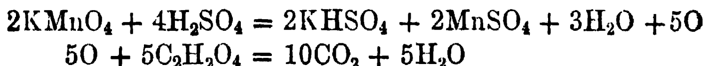
The above definition of a normal solution of an alkali still holds in such cases, *e.g.* normal sodium carbonate contains $\frac{1}{2}(46{\cdot}00 + 12{\cdot}00 + 48{\cdot}00) = 53{\cdot}00$ grams of the anhydrous salt per litre.

Normal Solutions of Oxidizing Agents.—A normal solution of an oxidizing agent, such as potassium permanganate or potassium bichromate, contains in 1 litre 1 gram-equivalent of oxygen, available for oxidation. Since exactly 16 grams of oxygen unite with or oxidize 2·016 grams of hydrogen or their equivalent of other substance, then the normal solution contains exactly 8 grams of oxygen available for oxidation. A typical oxidation by potassium permanganate in the presence of sulphuric acid is represented by—



$$2KMnO_4 + 4H_2SO_4 + 5H_2C_2O_4 = 2KHSO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

The weight of permanganate in grams is $2(39{\cdot}10 + 54{\cdot}93 + 64{\cdot}00) = 316{\cdot}06$. The number 316 is used as being more accurate than the experimental observations themselves. It will be observed on dissecting the equation thus—



$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5O + 5C_2H_2O_4 = 10CO_2 + 5H_2O$$

that only 5 of the 8 atoms of oxygen in the permanganate are available for oxidation. Hence the 316 grams of permanganate contain 80 grams of available oxygen. Therefore 31·6 grams of permanganate contain 8 grams of available oxygen, so that for oxidation in the presence of acid a normal solution contains 31·6 grams of potassium permanganate. From equations expressing its oxidizing

action upon oxalic acid, ferrous salts, etc., the amounts of oxalic acid, ferrous salts, etc., in any given solution may be calculated.

Normal Iodine Solution.—Iodine, dissolved in potassium iodide solution, is used for certain estimations. Since iodine is monovalent in the reactions concerned, a normal solution contains 126·92 grams of iodine per litre. Its action is really that of an oxidizing agent, and its estimation depends upon the reaction represented by

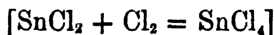


$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

In this reaction 1 molecule of sodium thiosulphate is equivalent to 1 atom of iodine. Therefore normal sodium thiosulphate will contain (46·00 + 64·00 + 48·00) = 158 grams of $Na_2S_2O_3$ per litre.

It must be noted that this normal solution contains two equivalents of sodium per litre, so that in other reactions it is possible for a solution containing only half the above amount of thiosulphate to be normal.

Normal Solutions of Reducing Agents.—Such solutions are those of stannous chloride, titanous chloride, oxalic acid, etc. They are normal when 1 litre of the solution is completely oxidized by the equivalent of oxygen (8 grams), or of chlorine (35·46 grams), *e.g.* normal stannous chloride could be made by dissolving $\frac{119 \cdot 0}{2}$ = 59·5 grams of tin in hydrochloric acid and making up to 1 litre.



$$[SnCl_2 + Cl_2 = SnCl_4]$$

Decinormal and Centinormal Solutions, etc.—Normal solutions are, as a rule, too concentrated for convenience. Weaker solutions are then employed, and, if one-tenth normal, are designated decinormal $\left(\frac{N}{10}\right)$. Similarly, one

hundredth normal $\left(\frac{N}{100}\right)$, half normal $\left(\frac{N}{2}\right)$, and other strengths are used.

It is not always convenient to make up solutions which are exactly normal or decinormal, and in such cases, when the concentration of the solution has been determined, it may be expressed by means of a factor, *e.g.* a 0·997 N. sulphuric acid contains 0·997 × 49·04 grams of sulphuric acid per litre. If a volume of, say, 10·45 c.c. of this solution has been taken, it is equivalent to 10·45 × 0·997 = 10·42 c.c. of normal acid.

EXAMPLES.—A solution of copper sulphate was electrolyzed, producing copper and sulphuric acid. The weight of the copper obtained was 0·1463 gram, and the sulphuric acid produced neutralized 15·62 c.c. of an alkali. What was the normality of the alkali?

1 gram-atom (63·57 grams) of copper is equivalent to 1 gram-molecule of sulphuric acid, which is equivalent to 2000 c.c. of N. alkali.

∴ 0·1463 gram of copper is equivalent to

$$\frac{2000 \times 0{\cdot}1463}{63{\cdot}57} \text{ c.c. N. alkali} = 4{\cdot}603.$$

Hence the

15·62 c.c. of the alkali are equivalent to 4·603 c.c. N. alkali
or 1·00 „ „ „ „ „ 0·2947 „ „
i.e. the normality of the alkali (the factor) is 0·2947.

11·382 grams of bleaching powder were suspended in a litre of water. 25·00 c.c. of this suspension, on treatment with dilute hydrochloric acid and potassium iodide liberated iodine, which required 24·37 c.c. of 0·1007 N. $Na_2S_2O_3$. What is the percentage of available chlorine in the bleaching powder?

1 c.c. N. $Na_2S_2O_3$ is equivalent to 1 c.c. N. I., which is equivalent to 1 c.c. N. Cl, *i.e.* to $\frac{35{\cdot}46}{1000}$ gr. Cl.

∴ 1 c.c. of 0·1007 N. $Na_2S_2O_3$ is equivalent to

$$\frac{35 \cdot 46}{1000} \times 0 \cdot 1007 \text{ gr. Cl,}$$

∴ 24·37 c.c. of 0·1007 N. $Na_2S_2O_3$ are equivalent to

$$\frac{35 \cdot 46}{1000} \times 0 \cdot 1007 \times 24 \cdot 37 \text{ gr. Cl,}$$

which is therefore the amount of chlorine in the 25 c.c. of bleaching powder solution. In the litre there were therefore—

$$\frac{1000}{25} \times \frac{35 \cdot 46}{1000} \times 0 \cdot 1007 \times 24 \cdot 37 \text{ grams of chlorine,}$$

and the percentage of available chlorine in the bleaching powder is therefore—

$$\frac{1000}{25} \times \frac{35 \cdot 46}{1000} \times 0 \cdot 1007 \times 24 \cdot 37 \times \frac{100}{11 \cdot 382} = 30 \cdot 57.$$

1. A quantity of ammonium chloride is boiled in an open vessel with 100 c.c. of normal sodium hydroxide until no further chemical change takes place; it is then found that the excess of sodium hydroxide requires 10 c.c. of normal sulphuric acid to neutralize it. How much ammonium chloride was used? (H = 1, N = 14, O = 16, S = 32, Cl = 35·5, Na = 23.)

(1st "Conjoint," July, 1909.)

2. What weight of sodium hydroxide would be required to neutralize 100 c.c. of a normal solution of sulphuric acid? What volume of carbon dioxide, measured at 15° C. and 760 mm., would be required to convert completely the above amount of sodium hydroxide into sodium bicarbonate?

(1st "Conjoint," January, 1909.)

3. 10 c.c. of a solution of ammonium chloride having a density of 1·011 gave on the addition of silver nitrate solution 0·9491 gram of silver chloride; calculate the amount of NH_4Cl in 100 grams and in 100 c.c. of the solution. How would you determine the amount of ammonia in 10 c.c. of the solution,

and how many c.c. of $\frac{N}{10}$ acid ought it to neutralize? (H = 1, N = 14, Cl = 35·5, Ag = 108.)

(London Inter. Hons., Extl., 1904.)

4. What amount of $KMnO_4$ must be dissolved in a litre in order that 1 c.c. of the solution may yield (*a*) 1 milligram of oxygen, (*b*) 1 c.c. of oxygen at N.T.P. in acid solution?

(Laboratory Paper, Manc.)

5. If 100 c.c. of a solution of sulphurous acid just decolourize 10 c.c. of a decinormal solution of iodine, what volume of sulphur dioxide does the solution contain?

(Laboratory Paper, Manc.)

6. To neutralize 10 c.c. of dilute hydrochloric acid, 40 c.c. of normal sodium hydroxide were required. In another 10 c.c. of the same acid, 1 gram of precipitated chalk ($CaCO_3$) was dissolved, and it was then found that 20·5 c.c. of normal sodium hydroxide were required to neutralize the excess of hydrochloric acid. Calculate the percentage of pure calcium carbonate in the precipitated chalk. (H = 1, C = 12, O = 16, Na = 23, Cl = 35·5, Ca = 40.)

(1st "Conjoint," January, 1910.)

7. 5·5502 grams of fuming sulphuric acid were dissolved in water and made up to 250 c.c. 50 c.c. of this solution required 52·05 c.c. of $\frac{N}{2}$ alkali. Express the composition of the original acid in percentages by weight of hydrogen sulphate and sulphur trioxide.

8. A solution contained sodium hydroxide and sodium peroxide. 100·0 c.c. were neutralized by 21·26 c.c. of N. sulphuric acid, and decolourized 16·6 c.c. of $\frac{N}{10}$ permanganate in the presence of sulphuric acid. How much sodium was present in 100 c.c. of solution, (1) as hydroxide, and (2) as peroxide?

(Leeds Univ., B.Sc., 1911.)

9. On treatment with a slight excess of water, 1 gram of a commercial sample of calcium carbide gave 290 c.c. of moist gas at 13° C. and 752 mm. pressure. (Pressure of aqueous vapour = 11 mm.)

In order to neutralize the residue 29 c.c. of normal hydrochloric acid were required.

(H = 1, C = 12, Ca = 40. 1 litre of hydrogen at 0° C. and 760 mm. weighs 0·09 gram.)

Calculate from the above data two independent values for the percentage of calcium carbide in the sample and explain the discrepancy in the results obtained.

(London Inter Hons., Extl., 1907.)

10. An orange-coloured gas was found to be absorbed by water, the solution then containing nitrous and hydrochloric acids. When 223 c.c. of the gas were absorbed by water, one-tenth of this solution, when titrated with permanganate in the cold, required 0·0632 gram $KMnO_4$; another tenth of the solution required 10 c.c. of decinormal $AgNO_3$ to precipitate the chlorine. On heating potassium in it the gas became colourless, and on cooling contracted to half its original volume. Find the formula of the gas. (1st Year Hons., Manc.)

11. Air containing chlorine and vapour of hypochlorous acid was passed for some time through an excess of $\frac{N}{10}$ sodium arsenite solution. The resulting solution was divided into two equal parts, the arsenite in one being determined by titration with iodine, the chloride in the other being determined by titration with silver nitrate. The arsenite oxidized being represented by 9·15 c.c. of $\frac{N}{10}$ iodine, and the chloride produced by 7·27 c.c. of $\frac{N}{10}$ silver nitrate, calculate what percentage of the total chlorine in the air is present (*a*) in the free state, (*b*) as hypochlorous acid? (R. L. Taylor, *J.C.S.*, 1910, **97**, 2541.)

CHAPTER X

ORGANIC ANALYSIS

Empirical Formulæ.—The first step in the full quantitative analysis of a pure organic substance is the determination of the proportions of the constituent elements separately.

Carbon and hydrogen are estimated by weighing separately the carbon dioxide and water produced when a weighed quantity of the substance is burnt. Thus 0·1836 gram of a substance produced on combustion 0·1934 gram of carbon dioxide and 0·0693 gram of water. Since carbon dioxide contains $\frac{12 \cdot 00}{44 \cdot 00}$ of its weight of carbon, the carbon present in the original substance was $\frac{12}{44} \times 0 \cdot 1934 = 0 \cdot 05275$ gram. Similarly the hydrogen present in the original substance was $\frac{2}{18} \times 0 \cdot 0693 = 0 \cdot 00770$ gram.*

Nitrogen is estimated from a measurement of the volume of free nitrogen produced when a weighed amount of the substance is burnt, special precautions being taken to ensure that the nitrogen is all liberated as such. Certain classes of nitrogenous substances may be so treated that their nitrogen is converted into ammonia, and estimated by passing into a measured amount of standard

* The use of $\frac{2}{18}$ or simply $\frac{1}{9}$ instead of $\frac{2 \cdot 016}{18 \cdot 016}$ introduces an error of 8 parts in 1110. This may be neglected, since the analytical figures are liable to much greater errors.

acid solution (Kjeldahl); in other cases the nitrogen may be converted completely into nitric oxide and measured as such (Lunge's "nitrometer" method).

Sulphur is converted into barium sulphate, and weighed as such. The halogens are converted into the corresponding silver halides.

In each case the calculation of the percentage composition from the analytical results presents no difficulty that has not been met in earlier chapters; from the percentage composition the empirical formula is deduced as shown in Chapter VI. In many of the exercises which follow it will be found unnecessary to express the analytical results as percentages, as the following example shows:—

A body contains only carbon, hydrogen, and oxygen. 0·2427 gram of it gives on combustion 0·3553 gram of carbon dioxide and 0·1461 gram of water. What is its simplest (empirical) formula?

In the 0·2427 gram are

$$0{\cdot}3553 \times \tfrac{3}{11} = 0{\cdot}0969 \text{ gram of carbon}$$

$$\text{and } 0{\cdot}1461 \times \tfrac{1}{9} = 0{\cdot}0162 \text{ gram of hydrogen}$$

Hence the total burnt, minus the hydrogen, minus the carbon, is the amount of oxygen in the substance, *i.e.* 0·1296 gram.

These are the relative quantities of carbon, hydrogen, and oxygen present; hence, by dividing each by the corresponding atomic weight, the relative numbers of atoms are found (Chapter VI.), *i.e.*—

$$\frac{0{\cdot}0969}{12} : \frac{0{\cdot}0162}{1} : \frac{0{\cdot}1296}{16} = 0{\cdot}00807 : 0{\cdot}0162 : 0{\cdot}0081$$

$$= 1 : 2 : 1$$

Hence the simplest formula is CH_2O.

Molecular Formulæ.—The molecular formula is, of course, either the same as the empirical formula or some

simple multiple of it. Molecular formulæ are deduced by one or other of the following methods for determining molecular weights :—

(I.) Measurement of the vapour density of the substance or of some substance made from it by a simple process.

Thus acetic acid has the empirical formula CH_2O ; its vapour density shows a molecular weight approximately 60 ; hence the molecular formula is $C_2H_4O_2$, which is twice the empirical formula.

Oxalic acid has the empirical formula CHO_2. It decomposes partially on vaporization, so that a vapour density determination is valueless. But methyl oxalate, by analysis and vapour density determination, is shown to have the molecular formula $C_4H_6O_4$, or $C_2(CH_3)_2O_4$; and since it is known to have been formed from oxalic acid by the replacement of hydrogen (H) by methyl (CH_3), the molecular formula of oxalic acid is probably $C_2H_2O_4$, twice the empirical formula.

(II.) Depression of freezing point and elevation of boiling point methods (see Chapter XII.).

(III.) Special method for an acid.

If the basicity of the acid (the number of atoms of hydrogen in the molecule which can be replaced by sodium on treatment with sodium carbonate) is known, then the silver salt is made and the proportion of silver in it determined by igniting in air and weighing the residue. The molecular weight of the acid is then given by—

$$\frac{\text{Weight of silver salt used}}{\text{Weight of silver produced}} = \frac{\text{molecular weight of acid} - n + n \, . \, 108}{n \, . \, 108}$$

where n is the basicity.

Thus lactic acid has the empirical formula CH_2O. It

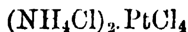
is monobasic, and its silver salt contains 54·8 per cent. silver. Hence

$$\frac{100 \cdot 0}{54 \cdot 8} = \frac{\text{molecular weight of lactic acid} - 1 + 108}{108}$$

∴ Molecular weight of acid = 90, which corresponds with the formula $C_3H_6O_3$, three times the empirical formula.

(IV.) Special method for a base.

Organic bases, such, for example, as methylamine, CH_3NH_2, form salts in the same way as ammonia, so that methylamine forms methylamine hydrochloride, $CH_3.NH_2.HCl$. Then, just as ammonium chloride forms an easily prepared double salt—



$$(NH_4Cl)_2.PtCl_4$$

so methylamine hydrochloride forms a double salt—



$$(CH_3.NH_2.HCl)_2.PtCl_4$$

Such salts, on ignition, leave a residue of pure platinum. The molecular weight of the base is obtained in a similar way to the determination in the previous example, *i.e.*—

$$\frac{\text{Weight of platinum salt}}{\text{Weight of platinum formed}} = \frac{2 \times \text{molecular wt. of base} + 2(1 + 35 \cdot 5) + 195 + 142}{195}$$

Constitutional Formulæ.—When the molecular formula has been determined, other data may enable the constitutional formula to be deduced; for these a text-book on organic chemistry must be consulted. They receive illustration in many of the following examples.

1. A substance containing carbon, hydrogen, and oxygen gave on combustion the following results: substance, 0·32; CO_2, 0·44; H_2O, 0·36. What is the simplest formula for the substance, and by what tests would you determine its nature?

(Inter. B.Sc., Manc.)

2. If 0·360 gram of an organic compound which contains only carbon, hydrogen, and oxygen yields on combustion 0·528 gram of carbon dioxide and 0·216 gram of water, what is its empirical formula? (C = 12.)

(1st "Conjoint," Sept., 1909.)

3. A substance containing only carbon, hydrogen, and oxygen was found by analysis to contain C = 52·15, H = 13·1 per cent.; a vapour density determination gave $\Delta = 23$. Determine the molecular formula of the substance.

(Inter. B.Sc., Manc., 1909.)

4. 0·37 gram of a substance containing carbon, hydrogen, and oxygen gave on combustion 0·66 gram of CO_2 and 0·27 gram of water. Further, 0·123 gram of the substance displaced 39·6 c.c. of air at 17° C. and 760 mm. in a determination of its vapour density by the Victor Meyer method. Ascertain from these data the molecular formula of the substance. (A litre of hydrogen at N.T.P. weighs 0·09 gram.)

(Inter. B.Sc., Manc., 1906.)

5. A liquid containing C, H, and O gave on analysis the following results: 0·1746 gram gave 0·3492 CO_2 and 0·1426 gram H_2O. The vapour density of the substance was found to be 22. (H = 1.) Find the formula of the liquid.

(General Organic, Manc.)

6. The analysis of an organic substance gave the following results: 0·2115 gram on complete combustion gave 0·4655 gram of carbon dioxide and 0·2533 gram of water. The vapour density of the substance was 29·7. Calculate the molecular formula, and give the names of the substances possessing this formula. (London Inter., Intl., 1908.)

7. 0·1027 gram of a substance gave on combustion 0·2178 CO_2 and 0·0303 H_2O. 0·1130 gram gave 0·0643 AgBr. What is the simplest possible empirical formula of the substance?

(General Organic, Manc.)

8. A substance gave the following results on analysis:—

(*a*) 0·1836 gram gave by combustion 0·1934 gram of CO and 0·0693 gram of H_2O.

(*b*) 0·3212 gram gave 0·3616 gram of AgBr.

What is the simplest formula for this substance?

(Bd. of Ed., Stage I., Organic, 1905.)

9. A dibasic acid containing only carbon, hydrogen, and oxygen was found by analysis to contain C 26·7 per cent., H 2·2 per cent.

A determination of the vapour density of its dimethyl ester gave $\Delta = 59$. What is the acid? (Inter., Manc., 1910.)

10. A substance gave the following results on analysis:—

0·2500 gave 0·6027 CO_2 and 0·339 H_2O

0·2000 gave 33·4 c.c. of nitrogen at 20° and 750 mm.

Its vapour density compared with hydrogen was 37. Calculate the composition of the substance and give the constitutional formulæ of the possible substances of this composition.

(Bd. of Ed., Stage II., Organic, 1907.)

11. A ketoxime, on analysis, was found to possess the following composition:—

Carbon, 55·2; hydrogen, 10·3; nitrogen, 16·1 per cent.

What is the formula of this compound and from what ketone is it derived? (Bd. of Ed., Stage II., Organic, 1910.)

12. A substance gave the following results on analysis:—

(*a*) 0·1836 gram gave, on combustion, 0·2241 gram of CO_2 and 0·0420 gram of H_2O.

(*b*) 0·3212 gram gave 0·3736 gram of AgBr.

What is the simplest possible formula for the substance?

(General Organic Class, Manc.)

13. Two liquids, one boiling at 83° C. and the other at 57° C., gave, on analysis, the same results, viz. 0·2376 gram gave, on combustion, 0·2112 CO_2 and 0·0864 H_2O; 0·121 gram gave, when heated with silver nitrate and nitric acid, 0·351 AgCl. Calculate the simplest formula for these substances. How do you account for two substances having the same composition, and what do you regard as the true formula of each compound?

(C = 12, Cl = 35·5, Ag = 108.)

(London Inter. Hons., Extl., 1904.)

14. A substance gave the following results on analysis:—

0·197 gram gave 0·293 gram CO_2 and 0·150 gram H_2O.

By the Kjeldahl method 0·59 gram required 10 c.c. of N. H_2SO_4 for neutralization of the ammonia. The original substance, when boiled with caustic soda, evolved ammonia, and the dry residue, heated with soda lime, gave off methane. What is the substance? (Leeds Univ., Genl. Organic, 1909.)

15. Calculate the formula of the aliphatic dicarboxylic acid which gave the following results on analysis:—

0·1340 gave 0·1760 CO_2 and 0·0540 H_2O.

(Lond. Scholarships, 1910.)

16. 0·2543 gram of a liquid hydrocarbon gave, on combustion, 0·8513 gram CO_2 and 0·1991 gram H_2O; a vapour density determination gave $D = 46$. Find its empirical formula. The hydrocarbon, on oxidation, gave an acid of the empirical formula $C_7H_6O_2$. Find the structural formula of the hydrocarbon. (Organic Class, Manc.)

17. The combustion of 0·246 gram of a liquid hydrocarbon yielded 0·792 gram of carbon dioxide and 0·270 gram of water. The hydrocarbon absorbed bromine readily, and yielded a compound containing 79·6 per cent. of bromine. From these data, what conclusions do you draw as to the formula of the hydrocarbon? ($C = 12$, $O = 16$, $Br = 80$.)

(London Inter., Veterinary Science, 1909.)

18. 0·2 gram of an anhydrous acid gave, on combustion, 0·040 gram H_2O and 0·195 gram CO_2. The acid is found to be dibasic, and 0·5 gram of the silver salt leaves, on ignition, 0·355 gram silver. What is the simplest formula for the acid, and what is its molecular formula?

(Organic Class, Manc.)

19. A mono-acid organic base gave the following results on analysis:—

0·100 gram gave 0·2882 gram CO_2 and 0·0756 gram water.

0·200 gram gave 21·8 c.c. nitrogen at 15° and 760 mm.

0·400 gram of the platinichloride left, on ignition, 0·125 gram of platinum.

What is the molecular formula of the base?

20. Certain white crystals having, in aqueous solution, a strongly acid reaction were found to consist of $H = 4·76$

C = 19·05, O = 76·19 per cent.; what is the simplest formula which would express the results of the analysis? Is this the formula adopted for the compound? If not, why not?
(London B.Sc. Pass, Extl., 1904.)

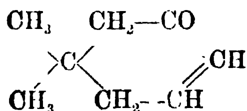
21. A hydrocarbon of the formula C_8H_{10} yields, on oxidation, a colourless crystalline dibasic acid, containing 57·8 per cent. of carbon, 3·6 per cent. of hydrogen. The silver salt contains 56·8 per cent. of silver. On heating the acid it is converted into a compound of the formula $C_8H_4O_3$; on distillation with lime, benzene is formed. Discuss the structure of the original hydrocarbon. (B.Sc., Manc.)

22. The monocyclic carbon compound A containing only carbon, hydrogen, and oxygen gave the following numbers on analysis: 0·1120 gave 0·2638 CO_2 and 0·0720 H_2O. When heated with ethyl alcohol and 5 per cent. sulphuric acid, A was converted into a substance containing C = 68·46, H = 8·67.

When A was treated with bromine in chloroform solution, bromine was absorbed, hydrogen bromide evolved, and a compound produced containing Br = 41·78 per cent. With hydroxylamine hydrochloride A gave a substance containing N = 19·84 per cent. (H = 1, C = 12, N = 14, O = 16, Br = 80).

What information can you deduce from these data regarding the presence of any particular groupings in A, and what formula can you suggest which would be in accord with the observed facts? (London Hons., Extl., 1909.)

23. A substance of the formula



on oxidation with potassium permanganate gave a product which was analyzed with the following results:—

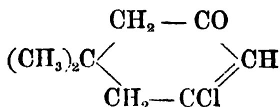
0·111 gave 0·2142 CO_2 and 0·0654 H_2O.

0·2019 required 12·85 c.c. of $\frac{N}{10}$ sodium hydroxide for neutralization in the cold and a further 11·9 c.c. on warming.

What structural formula would you assign to this oxidation product? (London Hons., Extl., 1908, adapted.)

24. The ammonium salt of a non-nitrogenous organic acid gave the following results on analysis: 0·2856 gram gave 0·3102 gram CO_2 and 0·180 gram H_2O, and 0·1562 gram gave 22·1 c.c. of dry nitrogen at 13° C. and 779 mm. pressure. Find the simplest formulæ for the salt and for the acid. (H = 1, C = 12, N = 14, O = 16; 1 litre of nitrogen at N.T.P. weighs 1·25 gram.) (London Hons., Extl., 1907.)

25. A ketone having the formula



was reduced by means of sodium in absolute alcoholic solution; 0·1499 gram of the resulting compound (A) gave, on combustion, 0·3835 gram CO_2 and 0·1559 gram H_2O. When treated with benzoyl chloride A was converted into a substance B, which contained 73·75 per cent. of carbon and 8·85 per cent. of hydrogen. What are the most probable formulæ for A and B? Explain the reactions by which they were produced? (London Hons., Extl., 1907.)

26. An acid, derived from *p*-xylene, gave the following results on analysis: 0·162 gram gave 0·4015 CO_2 and 0·1430 H_2O. When treated with bromine, it was converted into a bromo-derivative containing 36·2 per cent. of bromine, and this, when digested with alcoholic potash, yielded an acid which gave the following results on analysis: 0·17 gave 0·4276 CO_2 and 0·1309 H_2O. Assign constitutional formulæ to these acids, stating your reasons for their selection.

(B.Sc. Hons., Manc., 1905.)

27. A dibasic acid gave, on analysis, the following results: 0·1740 gram gave 0·3388 gram CO_2 and 0·1008 gram H_2O. When it was treated with bromine it yielded a dibromo derivative which gave, on analysis, C = 26·4, H = 3·2, Br = 50·3. Oxidation with permanganate converted the

dibasic acid into dimethyl malonic acid and oxalic acid. What is the constitution of the acid?

(B.Sc. Hons., Manc., 1906.)

28. An organic acid gave the following results on analysis: 0·1792 gave 0·3826 CO_2 and 0·1370 H_2O. The silver salt contained 43·0 per cent. of silver, and the oxime yielded 8·8 per cent. of nitrogen. What constitutional formulæ may the acid have, and how would you distinguish between them?

(B.Sc. Hons., Manc., 1907.)

29. A cyclic hydroxy-monobasic acid yielded on analysis the following results: 0·1800 gave 0·3854 CO_2 and 0·1346 H_2O. When this acid was treated with dehydrating agents, water was eliminated and an unsaturated acid formed which gave, on analysis, C = 66·7, H = 7·9.

Oxidation converted this unsaturated acid into γ-acetobutyric acid, $CH_3.CO.CH_2.CH_2.CH_2.CO_2H$. Discuss the constitutions of the hydroxy-acid and the unsaturated acid.

(B.Sc. Hons., Manc., 1911.)

30. An organic acid gave the following results on analysis: 0·1531 gram gave 0·3883 gram of carbon dioxide and 0·1410 gram of water. The silver salt gave 41·1 per cent. of silver, and when the acid was heated with bromine and afterwards with alcoholic potash it gave an acid containing 70·1 per cent. of carbon and 9·1 per cent. of hydrogen. The latter on heating with sulphuric acid was converted into an aromatic acid which yielded *m*-xylene on distillation with lime. Suggest formulæ for the three acids. (Inst. Chem., July, 1908.)

31. The ethyl ester of a dibasic acid, to which a normal carbon chain is assigned, has the composition: C = 61·11; H = 9·26; O = 29·63 per cent. When heated at 120° with sodium and a trace of alcohol, this ester is converted into a substance A of the composition: C = 63·53; H = 8·23; O = 28·24 per cent. From A, when boiled with dilute sulphuric acid, a second substance B is obtained of the composition: C = 73·47; H = 10·20; O = 16·33 per cent., the oxime of which contains N = 12·39 per cent. What is the probable constitution of B? (B.Sc. Hons., Lond., 1911.)

CHAPTER XI

THERMOCHEMISTRY

THERMOCHEMISTRY is the study of the heat effects accompanying chemical reaction. The union or reaction of two or more substances is accompanied by the liberation or absorption of a definite amount of energy, usually in the form of heat. From this circumstance, chemical reactions and compounds are distinguished as exothermic and endothermic. Exothermic reactions are accompanied by evolution, endothermic by absorption, of heat. Exothermic compounds are formed from their elements with evolution, endothermic compounds with absorption, of heat.

Units.—Quantity of heat is measured in calories, a calorie being defined as the amount of heat required to raise 1 gram of water through 1° C.* This unit is inconveniently small for chemical purposes so that it is customary to use the "large" calorie which is one thousand times as great as the small calorie, and is the amount of heat required to raise 1 kilogram of water through 1° C. To distinguish between the two units, gram calories are usually written cal.; kilogram calories, Cal. There is also the unit of heat (K) used by Ostwald which is the quantity

* This amount is not exactly the same for all intervals of one degree. A more precise definition stipulates that the water shall be warmed from 15·5° to 16·5°. Variation in the magnitude of the calorie with the particular portion of the temperature scale which is being considered is too small to enter into ordinary calculation.

of heat required to raise 1 gram of water from 0° to 100° C., and is very nearly equal to 100 small calories.

Ostwald also uses the joule, which is 10,000,000 ergs, and equal to $\frac{1}{4 \cdot 18}$ small calories, as the unit of heat. Thus 1 calorie = 4·18 joules, and 1 Calorie = 4·18 kilo-joules (*kj.*).

Nomenclature.—When by suitable means a determination has been made of the heat change in a given chemical reaction, the result is represented in a thermochemical equation, *e.g.*—



$$Zn + O = ZnO + 86{\cdot}4 \text{ Cal.}$$

i.e. 65·4 grams of zinc combine with 16 of oxygen to form 81·4 grams of zinc oxide, the heat evolution being 86·4 large calories.* The quantity 86·4 is called the heat of reaction between zinc and oxygen, the heat of combustion of zinc or the heat of formation of zinc oxide. The above equation is often abbreviated to (Zn, O) = +86·4.

Laws.—The basis of thermochemistry is an application of the doctrine of the conservation of energy to chemical phenomena, *e.g.* Lavoisier and Laplace arrived at the conclusion that the decomposition of a compound into its constituents absorbs exactly the same amount of heat as is evolved during its formation from those constituents. Thus the decomposition of zinc oxide is represented as an endothermic reaction by the thermochemical equation—



$$ZnO = Zn + O - 86{\cdot}4 \text{ Cal.}$$

so that the members of a thermochemical equation may be transposed in the same way as the members of an algebraic equation.

* Thermochemical equations are generally reduced to the simplest possible form, the above expression, for instance, being preferred to the more precise chemical equation $2Zn + O_2 = 2ZnO$. Thus Zn + O = ZnO + 86·4 Cal. indicates the *total* thermal change due to the union of

G. H. Hess, in 1840, extended the conception by formulating a law which states that the total heat effect of a chemical action is the same whether the reaction proceeds in one stage or in several, so long as the initial and final states are the same. For instance—



$$H + Cl = HCl + 22\ Cal.$$

If, however, the hydrogen chloride is produced by means of the following processes:—



$$H + Br = HBr + 13{\cdot}5\ Cal.$$



$$HBr + Cl = HCl + Br + 8{\cdot}5\ Cal.$$

it will be noted that the sum of these two equations—



$$H + Cl = HCl + 22\ Cal.$$

representing the net thermal and chemical effect, is identical with the above.

The truth of this law for all cases in which it has been tested leads to its application in determining the heat evolved in reactions which cannot be conducted under conditions suitable for measurement. For instance, from the data—



$$C + O_2 = CO_2 + 97{\cdot}0\ Cal.$$



$$CO + O = CO_2 + 68{\cdot}2\ Cal.$$

it is deduced, by subtracting the second equation from the first, that—

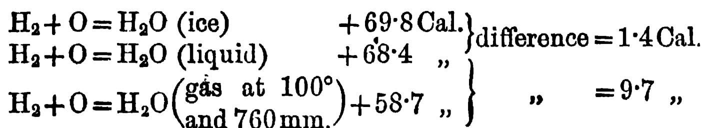


$$C + O = CO + 28{\cdot}8\ Cal.$$

Influence of Physical State.—It must be remembered that since heat changes also accompany processes which are not chemical (*e.g.* melting, boiling), it is necessary to know the conditions under which the reaction has been carried out. The magnitude of the error which may be

65·4 grams of zinc with 16 grams of oxygen. No attempt is made to indicate what part of the heat effect is due to the dissociation of oxygen molecules, and what part is due to the union of zinc atoms with oxygen atoms, or the volatilization of the zinc or the condensation of zinc oxide.

incurred by neglect of this is illustrated by the following equations:—



$$H_2 + O = H_2O \text{ (ice)} \quad +69{\cdot}8 \text{ Cal.}$$
$$H_2 + O = H_2O \text{ (liquid)} \quad +68{\cdot}4 \text{ ,,} \quad \text{difference} = 1{\cdot}4 \text{ Cal.}$$
$$H_2 + O = H_2O \left(\begin{array}{l}\text{gas at } 100^\circ \\ \text{and } 760 \text{ mm.}\end{array}\right) + 58{\cdot}7 \text{ ,,} \quad \text{,,} \quad = 9{\cdot}7 \text{ ,,}$$

The differences represent respectively the latent heat of fusion and the latent heat of vaporization of the gram-molecular weight of water.

In thermochemical equations the reagents are assumed to be in the state of aggregation in which they would exist at ordinary temperature and pressure, unless the contrary is stated.

Reactions in Aqueous Solution.—The thermal change due to the solution of substances in water must often be known for thermochemical calculations dealing with reactions in solution. A difficulty in dealing with this heat of solution is that it depends on the concentration of the resulting solution, as shown by the following numbers obtained by Thomsen for sulphuric acid dissolved in water:—

H_2SO_4, H_2O	...	6·38 Cal
$H_2SO_4, 2H_2O$	...	9·42 ,,
$H_2SO_4, 3H_2O$	...	11·14 ,,
$H_2SO_4, 19H_2O$	...	16·26 ,,
$H_2SO_4, 199H_2O$	...	17·06 ,,
$H_2SO_4, 799H_2O$	...	17·64 ,,
$H_2SO_4, 1599H_2O$	...	17·86 ,,

Obviously, if the solution is sufficiently dilute, the heat effect of further dilution is negligible, and the heat of solution of sulphuric acid at great dilution is expressed by the equation—



$$H_2SO_4 + aq = H_2SO_4aq + 17{\cdot}9 \text{ Cal.}$$

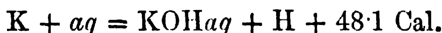
This is quite different from the following:—



$$H_2SO_4 + H_2O = H_2SO_4H_2O + 6{\cdot}4 \text{ Cal.}$$

which refers to the formation of a definite hydrate of sulphuric acid.

The symbol *aq* is a contraction for *aqua,* and means an indefinitely large amount of water; this is practically the same in thermal result as a moderately large excess of water. It is to be noted that *aq* may frequently enter into specific reactions besides those concerned with simple dilution, *e.g.*—



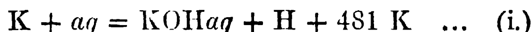
$$K + aq = KOHaq + H + 48{\cdot}1 \text{ Cal.}$$

where the thermal effect consists of the heat of reaction of potassium with water and the heat of solution of the resulting potassium hydroxide. If the equation is to be used algebraically it should be considered as—

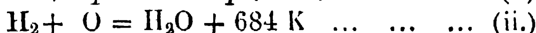


$$K + H_2O + aq = KOHaq + H + 48{\cdot}1 \text{ Cal.}$$

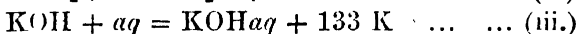
EXAMPLE.—Given



$$K + aq = KOHaq + H + 481 \text{ K} \quad \ldots \quad \text{(i.)}$$



$$H_2 + O = H_2O + 684 \text{ K} \quad \ldots \quad \ldots \quad \ldots \quad \text{(ii.)}$$



$$KOH + aq = KOHaq + 133 \text{ K} \quad \ldots \quad \ldots \quad \text{(iii.)}$$

Find the heat of formation of KOH from its elements (K, O, H).

(i.) may be written—



$$K + H_2O + aq = KOHaq + H + 481 \text{ K}$$

Also



$$H_2 + O = H_2O + 684 \text{ K}$$

By addition—



$$K + O + H + aq = KOHaq + 1165 \text{ K} \quad \ldots \quad \text{(iv.)}$$

(iii.) is—



$$KOH + aq = KOHaq + 133 \text{ K}$$

By subtracting (iii.) from (iv.)—



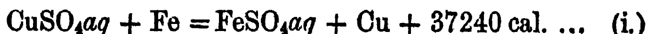
$$K + O + H - KOH = 1032 \text{ K}$$

or

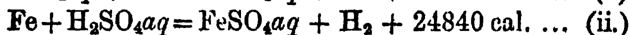


$$K + O + H = KOH + 1032 \text{ K}$$

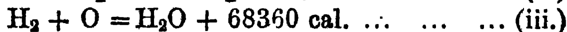
EXAMPLE.—Given



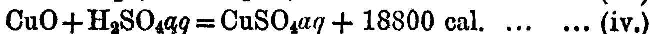
$$CuSO_4aq + Fe = FeSO_4aq + Cu + 37240 \text{ cal.} \quad \ldots \quad (i.)$$



$$Fe + H_2SO_4aq = FeSO_4aq + H_2 + 24840 \text{ cal.} \quad \ldots \quad (ii.)$$



$$H_2 + O = H_2O + 68360 \text{ cal.} \quad \ldots \quad \ldots \quad \ldots \quad (iii.)$$



$$CuO + H_2SO_4aq = CuSO_4aq + 18800 \text{ cal.} \quad \ldots \quad \ldots \quad (iv.)$$

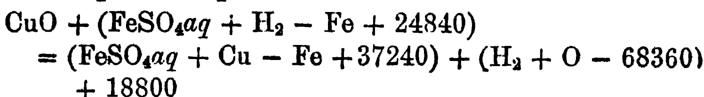
Find the heat of formation of CuO.

Equation (iv.) is—



$$CuO + H_2SO_4aq = CuSO_4aq + H_2O + 18800$$

By substitution from equations (ii.), (i.), and (iii.), for H_2SO_4aq, $CuSO_4aq$, and H_2O—



$$CuO + (FeSO_4aq + H_2 - Fe + 24840)$$
$$= (FeSO_4aq + Cu - Fe + 37240) + (H_2 + O - 68360)$$
$$+ 18800$$

Whence by cancelling—



$$CuO = Cu + O - 37160$$

or



$$Cu + O = CuO + 37160 \text{ cal.}$$

1. Given—



$$2I + Cl_2 = 2ICl + 11650 \text{ cal.}$$



$$ICl + Cl_2 = ICl_3 + 15660 \text{ cal.}$$

Find the heat of formation of ICl_3 from its elements.

2. On dissolving 100 grams of anhydrous copper sulphate in water, the heat evolved amounted to 9900 cals., whilst the same weight of crystallized copper sulphate ($CuSO_45H_2O$) gave an absorption of heat amounting to 1100 cals.: determine the heat of transformation of the gram-molecule of $CuSO_4$ into $CuSO_45H_2O$. (B.Sc. Hons., Manc., 1905.)

3. Anhydrous magnesium chloride is to be prepared from magnesia, chlorine, and carbon. The heat of combination of magnesium and oxygen, of magnesium and chlorine, and of carbon and oxygen are 145860, 151000, and 28600 respectively in gram-calories per [gram] molecule. Calculate the balance of gram-calories given out or absorbed.

(Inst. Chem., Inter., July, 1910.)

4. Find the heats of formation of the following hydrocarbons from their respective heats of combustion, given that

$[C, O_2] = 96960$ cal. and $[H_2, O] = 68360$ cal. Methane, 211930; ethane, 370440; ethylene, 333350; acetylene, 310059; benzene (vapour), 799350 cals. per gram-mol.

5. Calculate the molecular heat of reduction of ethylene to ethane, given the following data :—

Molecular heat of combustion of hydrogen	64·49	Calories.
„ „ „ ethane	369·0	„
„ „ „ ethylene	332·2	„

(Hons., Manc., 1910.)

6. From the following data calculate the thermal effect produced by the decomposition of ozone by hydrogen peroxide :—

$$(H_2, O) = 68,000 \text{ cals.}$$
$$(H_2, O_2) = 45,000 \text{ cals.}$$
$$(O_2, O) = -30,000 \text{ cals.}$$

(Hons., Vict., 1894.)

7. Calculate the heat of formation of formic acid from the following data :—

Heat of combustion of carbon $[C, O_2]$	= 96,960	cals.
„ „ hydrogen $[H_2, O]$	= 68,360	„
„ „ formic acid $[CH_2O_2, O]$	= 65,900	„

(2nd Year Hons., Manc., 1910.)

8. Find the heat of formation of aldehyde, (i.) gaseous, (ii.) liquid, from the following data :—

$$(2C_2H_4O, 5O_2) \text{ liquid} = 551 \text{ Cals.}$$
$$(2C_2H_4O, 5O_2) \text{ gaseous} = 564 \text{ „}$$
$$(C, O_2) = 97 \text{ „}$$
$$(2H_2, O_2) \text{ to water} = 136·7 \text{ „}$$

(B.Sc. Hons., Manc., 1908.)

9. Calculate the heat of combination of calcium and oxygen from the following equations :—



$$CaO + 2HCl = CaCl_2 + H_2O + 52·7 \text{ Cal.}$$



$$Ca + Cl_2 = CaCl_2 + 169·8 \text{ Cal.}$$



$$H_2 + O = H_2O + 57·9 \text{ „}$$



$$H + Cl = HCl + 22·0 \text{ „}$$

(Inst. Chem., July, 1907.)

10. Given—

$$[\text{Na}, aq] = 43{,}450 \text{ cal.}$$
$$[\text{H}, \text{Cl}] = 22{,}000 \text{ ,,}$$
$$[\text{HCl}, aq] = 17{,}314 \text{ ,,}$$
$$[\text{NaOH}aq, \text{HCl}aq] = 13{,}745 \text{ ,,}$$
$$[\text{NaCl}, aq] = -1180 \text{ ,,}$$

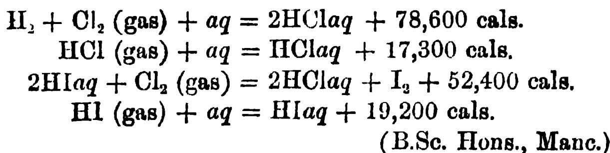
Find the heat of formation of sodium chloride from its elements.

11. From the following figures of Thomsen—

$$[\text{Fe}, 2\text{HCl}aq] = 21{,}320 \text{ cal.}$$
$$[\text{FeCl}_2aq, \text{Cl}] = 27{,}770 \text{ ,,}$$
$$[\text{FeCl}_2, aq] = 17{,}900 \text{ ,,}$$
$$[\text{FeCl}_3, aq] = 31{,}680 \text{ ,,}$$
$$[\text{H}, \text{Cl}] = 22{,}000 \text{ ,,}$$
$$[\text{HCl}, aq] = 17{,}314 \text{ ,,}$$

find the heats of formation of ferric and ferrous chlorides from their elements.

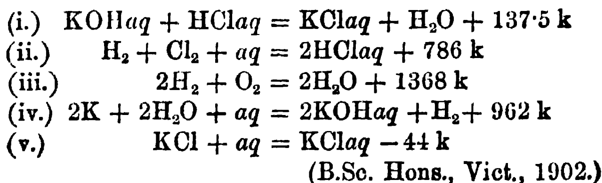
12. From the following data calculate the heats of formation of gaseous hydrochloric and hydriodic acids respectively from their elements :—



$$H_2 + Cl_2 \text{ (gas)} + aq = 2HCl aq + 78{,}600 \text{ cals.}$$
$$HCl \text{ (gas)} + aq = HCl aq + 17{,}300 \text{ cals.}$$
$$2HI aq + Cl_2 \text{ (gas)} = 2HCl aq + I_2 + 52{,}400 \text{ cals.}$$
$$HI \text{ (gas)} + aq = HI aq + 19{,}200 \text{ cals.}$$

(B.Sc. Hons., Manc.)

13. From the following data calculate the heat of formation of solid potassium chloride from its elements :—



(i.) $KOH aq + HCl aq = KCl aq + H_2O + 137{\cdot}5 \text{ k}$
(ii.) $H_2 + Cl_2 + aq = 2HCl aq + 786 \text{ k}$
(iii.) $2H_2 + O_2 = 2H_2O + 1368 \text{ k}$
(iv.) $2K + 2H_2O + aq = 2KOH aq + H_2 + 962 \text{ k}$
(v.) $KCl + aq = KCl aq - 44 \text{ k}$

(B.Sc. Hons., Vict., 1902.)

14. The heat of formation of hypochlorous acid has been determined by two independent methods by Thomsen; his

results are given below. From both sets calculate the heat of formation of an aqueous solution of the acid (H, Cl, O, *aq*).

A.	B.
(2NaOH*aq*, Cl_2) = 24,647,	(HClO*aq*, 2HI*aq*) = 51,435,
(NaOH*aq*, HClO*aq*) = 9,976,	(H, I, *aq*) = 13,171,
(NaOH*aq*, HCl*aq*) = 13,740,	

(H, Cl, *aq*) = 39,315,
(H_2, O) = 68,357.

(London Hons., Extl., 1907.)

15. In order to determine the heat of formation of ammonia, Thomsen passed chlorine into its aqueous solution, and found for the reaction [$4NH_3$*aq*, 3Cl] an evolution of 119,613 heat units; he also found for—

[H, Cl] = 22,001 [NH_3*aq*, HCl*aq*] = 12,270
[HCl, *aq*] = 17,314 [NH_3, *aq*] = 8,435

but afterwards by the combustion of ammonia he found—

[$2NH_3$, 3O] = 181,296
[H_2, O] = 68,357

Calculate the heat of formation of ammonia gas from each set of data, and compare and contrast the reliability and probable sources of error in each method.

(London Hons., Extl., 1905.)

16. Find the heat of formation of hydrogen sulphate from its elements from the following data :—

(H_2SO_3*aq*, H_2O, Cl_2) = H_2SO_4*aq* + 2HCl*aq* + 73,900 cal. (i.)
(H, Cl, *aq*) = HCl*aq* + 39,300 cal. ... ... (ii.)
(H_2, O) = H_2O + 68,400 cal. ... ... (iii.)
(SO_2, *aq*) = H_2SO_3*aq* + 7700 cal. ... ... (iv.)
(S, O_2) = SO_2 + 69,900 cal. ... ... (v.)
(H_2SO_4, *aq*) = H_2SO_4*aq* + 17,000 cal. ... ... (vi.)

17. From the following data, based on the use of semi-normal solutions throughout, calculate the heat which should be liberated in the production, in aqueous solution, of one gram-molecule of ammonium acetate. 250 c.c. of caustic soda

mixed with an equal volume of hydrochloric acid liberate 1710 calories; the same volumes of caustic soda and acetic acid liberate 1620 calories, and of ammonia and hydrochloric acid 1530 calories. For the purpose of the calculation it is assumed that, in the solutions employed, the caustic soda and hydrochloric acid are fully dissociated.

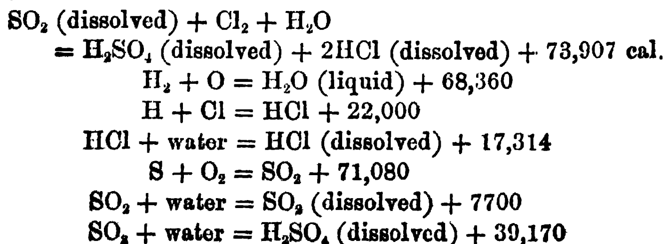
(B.Sc., Lond., 1910.)

18. 0·5599 gram of peat gave on combustion with excess of oxygen an evolution of 2521 calories of heat. Calculate (i.) the number of calories evolved by the combustion of one gram of peat; (ii.) the number of B.T.U.'s evolved by the combustion of 1 lb. of peat.

(B.T.U. means British Thermal Unit; it is the amount of heat required to raise the temperature of 1 lb. of water through 1° Fahr.)

19. A gaseous hydrocarbon was analyzed by explosion with the following result: 20 c.c. of hydrocarbon with 80 c.c. of oxygen gave 50 c.c. of residual gas, of which 40 c.c. were CO_2 and 10 c.c. O_2. When 2·86 litres of this hydrocarbon (measured over water at 13° C. and 751 mm.) were burnt in a Junker calorimeter, 2·6 litres of water were heated from an average temperature of 4° to an average temperature of 22°, and 5 c.c. of water were condensed from the products of combustion. Calculate the molecular heat of combustion (calories evolved by burning 22·4 litres) when the hydrogen of the hydrocarbon is burnt to steam and the carbon to carbon dioxide. Latent heat of steam 540 calories. Pressure of aqueous vapour at 13° = 11 mm. (B.Sc. Hons., Manc.)

20. Given—



SO_2 (dissolved) + Cl_2 + H_2O
= H_2SO_4 (dissolved) + 2HCl (dissolved) + 73,907 cal.

$H_2 + O = H_2O$ (liquid) + 68,360

$H + Cl = HCl + 22,000$

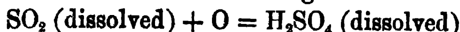
HCl + water = HCl (dissolved) + 17,314

$S + O_2 = SO_2 + 71,080$

SO_2 + water = SO_2 (dissolved) + 7700

SO_3 + water = H_2SO_4 (dissolved) + 39,170

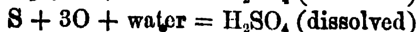
Find the thermal effect of the following reactions :—



$$SO_2 \text{ (dissolved)} + O = H_2SO_4 \text{ (dissolved)}$$

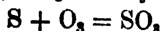


$$SO_2 + O + \text{water} = H_2SO_4 \text{ (dissolved)}$$



$$S + 3O + \text{water} = H_2SO_4 \text{ (dissolved)}$$

and



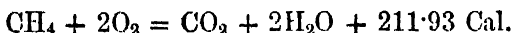
$$S + O_3 = SO_3$$

Heat of Reaction at Constant Pressure and Constant Volume.—Up to this point heat values have been expressed for reactions occurring at constant pressure, namely, atmospheric. If a chemical reaction at constant pressure results in the production of gas of different volume from that which was present initially, then work is done *by* the system if expansion has occurred, or *on* the system if contraction has occurred. Hence the heat evolution is respectively less or greater than that which would occur had no work been done.

The difference is frequently significant, especially in the case of the determination of heats of combustion. In the Berthelot bomb the reaction is performed at constant volume; in some other forms of calorimeter at constant pressure. It is useful, therefore, to be able to transform each value of the thermal effect of a reaction into the other. This is done as follows :—

The production of 1 gram-molecule of a gas at constant pressure necessitates the use of pv units of work (see text-book). Now, $pv = RT$, so the work done $= RT$, which in calories $= 2T$. Hence the production of n gram-molecules of gas involves work done by the gas equal to $2nT$ calories, where n may be positive or negative or zero.

EXAMPLE.—The combustion of methane at constant pressure—



$$CH_4 + 2O_2 = CO_2 + 2H_2O + 211{\cdot}93 \text{ Cal.}$$

at 15° C. (initial and final temperatures) has resulted in the absorption of $+ 2 \times 1 \times 288$ calories, *i.e.* $+ 0{\cdot}576$ Cal., on account of the *decrease* in volume of 1 gram-

molecule of gas (the water is assumed to be entirely condensed). Hence the heat of combustion of methane at constant volume = 211·93 − 0·576 = 211·35 Cal.

21. Find the heat of combustion at constant volume of ethane, ethylene, and acetylene, given that their heats of combustion at constant pressure are 370440, 333350, and 310059 calories respectively at 15° C.

22. Find the heat of combustion of benzene vapour at constant volume, given that its heat of combustion at constant pressure is 801·2 Cal. at 120° C.

Calorific Power.—The calorific power of a substance is the number of units of heat which unit amount of it (1 gram, 1 kilogram, 1 pound, 1 cubic foot, as the case may be) will produce on complete combustion. This term is used rather than "heat of combustion" for combustible substances which are not pure chemical compounds and whose oxidation cannot be represented in a single equation. As water is generally a product of the combustion of such a substance, a distinction is made between the *gross calorific power*, which includes the heat of condensation of the water, and the *nett calorific power* which corresponds to the formation of water vapour.

Calorific Intensity.—The calorific intensity of a reaction is the temperature attained in it on the assumptions (i.) that the reaction is complete before any heat is lost by radiation from the flame; (ii.) that the specific heats of the products of the reaction are known. The calorific intensity of a reaction, in degrees Centigrade,

$$= \frac{\text{total heat evolved}}{\text{heat required to raise the products through } 1^\circ \text{ C.}}$$

23. Calculate the gross calorific power of a cubic foot (at 0° and 760 mm.) of dry gas containing CO_2 = 13·2; CO = 15·3; H_2 = 19·5; CH_4 = 3·8; N = 48·2 per cent., assuming the following molecular heats of combustion:—

$H_2 + O = H_2O$ (water) = 68·4 kilogram-centigrade units.
$CO + O = CO_2$ = 68·0 " " " "
$CH_4 + 2O_2 = CO_2 + 2H_2O$ = 213·0 " " " "
[N.B. 1 cubic foot = 28·3 litres.] (Fuel, Manc., 1905.)

24. A regenerative furnace holds 10 crucibles, each containing 100 lbs. of steel. Assume—

(1) That the total heat in each lb. of steel when melted = 300 calories.

(2) That the furnace is fed by gas with a calorific power of 480 calories per cubic foot.

(3) That only 5 per cent. of the heat generated is used for melting the steel.

Required: The number of cubic feet of gas for melting 1 ton (= 2000 lbs.) of steel.

(Hons., Manc., Metallurgy, 1907.)

25. Calculate the temperature of the hydrogen flame burning in (*a*) oxygen, (*b*) dry air. Heat of combustion of 1 cubic metre of hydrogen is 2613 Calories. The mean specific heat of water vapour between 0° and $t° = 0·34 + 0·00015t$, and of oxygen and nitrogen $= 0·303 + 0·000027t$.

(Fuel Class. Manc., 1908.)

26. Calculate the calorific intensity of carbon burning in oxygen and in air respectively if (C, O_2) = 96960
specific heat of carbon dioxide = 0·2164
specific heat of nitrogen = 0·2438

Composition of air = 79 volumes of nitrogen and 21 volumes of oxygen. (London Pass B.Sc., Extl., 1903.)

CHAPTER XII

SOME PRINCIPLES OF PHYSICAL CHEMISTRY

THE examples of this chapter and of the previous one cover a great part of physical chemistry. The student who understands his text-book will find himself capable of solving most of them without further explanation; to attempt explanation would involve the writing of a text-book.

One point, derived from experience of teaching students, may be mentioned. It is, as a rule, safer and more permanently useful to work from principles than to memorize formulæ. Just as in correcting a gas volume to N.T.P., most experienced chemists seem to remember the principles and apply them as best fit the particular case, so, for example, in deducing a molecular weight from an observation of the depression of a freezing point, most chemists use the principles, but do not remember the formula. The difference is that instead of putting the principles into a formula and translating that to the particular case in point, the direct method is used.

A few of the following examples, more especially some of those in the sections on rate of diffusion of gases, solubility of gases, molecular weight determinations and electrochemistry, may be attempted by the junior student. He may choose those obtained from Intermediate B.Sc. papers, and some others.

Deviations from the Simple Gas Laws.

1. Guye found that the weight of a normal litre of the gas obtained by the decomposition of ammonia was 0·3799 gram.

Taking the weight of a normal litre of hydrogen as 0·0899 gram and the weight of a normal litre of nitrogen as 1·2507 gram, then—

(1) On the assumption that the gases obey Boyle's Law, calculate the combining volumes of nitrogen and hydrogen at 0° C. and the atomic weight of nitrogen.

(2) If, owing to deviations from Boyle's Law, the litre of nitrogen at 0° C. became 1·0004 litres when diluted with the 3 volumes of hydrogen, and the litre of hydrogen at 0° C. became 0·9999 litre when diluted with one-third of its volume of nitrogen, at atmospheric pressure, what effect would these deviations have on the determination? (Hons., Manc., 1910.)

2. Calculate the critical temperature and critical pressure of nitric oxide from the following equation:—

$$\left(p + \frac{0\cdot00257}{v^2}\right)(v - 0\cdot001156) = RT.$$

(Inst. Chem., Phys., 1910.)

Rate of Diffusion of Gases.

3. If 50 c.c. of hydrogen take 10 minutes to diffuse out of a vessel, how long will 20 c.c. of nitrogen take to diffuse under the same conditions? (H = 1, N = 14.)

(Bd. of Ed., Stage I., Inorg., 1910.)

4. If 50 volumes of hydrogen take 85 seconds to diffuse from a vessel, how long would it take 35 volumes of nitrous oxide to do so under the same conditions?

(London Pre. Sc., Vet., 1905.)

5. The relative rates of diffusion of oxygen, hydrogen, and nitrogen are respectively 0·96, 3·80, and 1·015. What deduction may be drawn from these figures concerning the density of nitrogen? (London Inter., Intl., 1908.)

6. Soret found that when chlorine mixed with oxygen, diffused through a small aperture into oxygen, the proportion

of the diffused chlorine to that remaining in the vessel in 45 minutes was represented by the number 0·2270; whilst in a similar experiment made with ozonized oxygen the proportion of the diffused ozone to that remaining in the vessel in 45 minutes was 0·2708. From these numbers determine the density of ozone (*a*) with chlorine as unity, and (*b*) with hydrogen as unity.

(London Inter., Veterinary Science, 1909.)

7. If, in Soret's apparatus, 100 c.c. of HCl gas had been mixed with oxygen and 18 c.c. had diffused in half an hour, what molecular weight would you assign to an acid gas of which 12 c.c. (out of 100 c.c.) diffused under the same conditions? (1st Year Hons., Manc.)

8. Two vessels, A and B, containing respectively chlorine and a mixture of oxygen with another gas, are connected by means of a short capillary tube. The mixture contains 10 per cent. of oxygen. After diffusion for a limited time, the chlorine in A is absorbed by potash, and the residual gas contains 11·05 per cent. of oxygen. What is the density of the second gas? (Hons., 1903, Manc.)

Solubility of Gases.

9. Air, containing 20·9 per cent. of oxygen, 79·0 per cent. of nitrogen, and 0·1 per cent. of carbon dioxide, is bubbled through water for half an hour. Calculate the composition of the mixture of gases which would be obtained on boiling the solution, given the following coefficients of solubility at the temperature of the water: oxygen = 0·040, nitrogen = 0·020, carbon dioxide = 1·79.

10. A natural water, on boiling, gave a mixture of gases of the following composition: oxygen = 20·9 per cent., nitrogen = 39·5 per cent., carbon dioxide = 39·6 per cent. Assuming that the water had dissolved these gases from the air with which it had previously been in contact, calculate the composition of that air. Use the coefficients of solubility given in the previous question.

11. One litre of a mixture of oxygen and carbon dioxide

in equal proportions by volume is shaken with 1 litre of water at 0° C. until equilibrium is established. The initial pressure is 760 mm. Calculate the final pressure and the composition of the residual gas. (The coefficients of absorption at 0° are: oxygen, 0·04; carbon dioxide, 1·79.)

(Inst. Chem., Inter., July, 1906.)

12. Water is shaken up with its own bulk of a mixture of 1 volume of nitrogen and 3 volumes of nitric oxide. Supposing the temperature and pressure to remain normal and constant throughout the experiment, calculate the composition of the residual gas. Bunsen's coefficient for nitrogen is 0·0235, and for nitric oxide, 0·0738.

(Inst. Chem. Phys., July, 1910.)

Molecular Weight Determinations—Osmotic Pressure—Freezing and Boiling Points and Capillarity.

13. Admitting the analogy between gaseous and osmotic pressures, calculate the osmotic pressure of a 1 per cent. cane sugar solution at 0°. (Leeds Univ., Phys. Chem.)

14. Calculate the osmotic pressure of an aqueous solution containing 5·00 grams of dissolved substance per litre given that the solution freezes at $-0·25°$ C. The molecular lowering of the freezing point of water may be taken as 18·5°.

(Leeds Univ., Physical Chem.).

15. 3·29 grams of a substance dissolved in 100 grams of water ($K = 19$) gave a depression of the freezing point of 2·04° C. Find the molecular weight of the substance.

(London Inter., Intl., 1908.)

16. Successive quantities of 0·317, 0·394, and 0·5152 gram of a substance were dissolved in 18·054 grams of benzene. The depressions of freezing point were 0·278°, 0·348°, and 0·452° respectively. What was the molecular weight of the substance? The molecular lowering of the freezing point of benzene is 50°. (Inst. Chem., July, 1902.)

17. The electrical conductivity of a 5 per cent. solution of chromium trioxide is not increased by further dilution, and its

freezing point is $-1{\cdot}34°$. What conclusions can you draw as to the condition in which the oxide exists in solution? (K = 19.) (Hons., Manc., 1907.)

18. A current of dried air was passed through a solution of 3·458 grams of a substance in 100 grams of ethyl alcohol, and then passed through ethyl alcohol alone. The loss in weight of the former liquid was 0·9675 gram, and of the alcohol 0·0255 gram. Find the molecular weight of the dissolved substance. (B.Sc. Hons., Manc., 1907.)

19. 2·012 grams of resorcinol are dissolved in 100 grams of ether. The rise in the boiling point is 0·399°. Find the molecular weight of the resorcinol, being given that the boiling point of ether is 34·8°, and the latent heat of vaporisation 84·5 calories. (Inst. Chem. Phys., 1910.)

20. Calculate the latent heat of fusion of tin from the following data: melting point of tin = 232° C. The depression of the freezing point for 1 gram-atom of silver per 100 gram-atoms of tin is 3·0° C. (London Hons., Intl., 1907.)

21. Show from the following data that the molecules of formic acid in the liquid state are associated, but that they gradually dissociate as the temperature rises.

Radius of capillary = 0·01425 cm.

Temperature	...	16·8	46·4	79·8° C.
Height of liquid	...	4·442	4·205	3·90 cm.
Density „	...	1·207	1·170	1·129

(Inst. Chem. Phys., 1909.)

22. On heating nitrocamphor (formula $C_{10}H_{15}NO_3$) only water is eliminated, and the other product gave the following results on analysis:—

0·3391 gram gave 21·8 c.c. of moist nitrogen at 19° and 767 mm.
0·4332 „ „ 28·2 „ „ „ 21° „ 760 „
0·1650 „ „ 0·3858 gram of carbon dioxide and 0·1138 gram of water.

The molecular weight was determined by the elevation of the boiling point of benzene.

2·8487 grs. raised the boiling point of 11·10 grs. of benzene							2·011°
1·8842	,,	,,	,,	,,	,,		1·214°
1·9012	,,	,,	,,	,,	,,		1·191°

Molecular elevation of boiling point for benzene = 26·7. What is the probable formula of the product?

(Lowry, *J.C.S.*, 1898, **73**, 997.)

Velocity of Reaction.

23. The spontaneous change of radium emanation, freshly drawn, is a monomolecular reaction. The results obtained were—

Time.	Volume.
0	0·102
7	0·062
11	0·044
14	0·033
16·5	0 025
20	0·019
25	0·016
36	0·007
45	0·003
64	0 002
75	0·000

Show how these figures fit the order of the reaction.

(London Hons., Intl., 1907).

24. Diazoamido benzene ($C_6H_5.NH.N_2C_6H_5$) is converted into amidoazobenzene ($C_6H_5N_2.C_6H_4NH_2$) under the influence of aniline hydrochloride. The former compound liberates two-thirds of its nitrogen when boiled with dilute acids; the latter gives no nitrogen under these conditions. The progress of the reaction was therefore followed by withdrawing from time to time a weighed portion of the reaction mixture and determining the volume of nitrogen evolved. From the following results of a series of measurements show that the reaction is monomolecular. The original mixture consisted of 0·6475 gram of aniline hydrochloride, 4·925 grams of

diazoamidobenzene and 50 grams of aniline, which acted as solvent.

Time (in hours).	Weight of sample.	C.c. of moist N_2.	Bar.	Temp.
18·11	2·645	22·8	750	14·0°
66·25	5·255	21·8	748	12 5°
115·2	5·940	12·9	753	8·5°

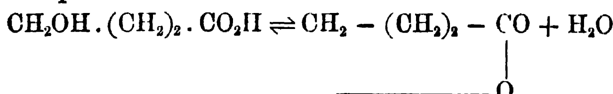
(Inst. Chem., Phys., July, 1911.)

25. In an investigation of the reaction between hydrogen peroxide and hydriodic acid the following results were obtained:—

Experiment I.	Concentration of HI, 0·02;	of H_2O_2, 0·02
„ II.	„ , „ 0·01;	„ 0·01
„ III.	„ „ „ 0·005;	„ 0·005

The times taken for the completion of one-fourth of the reaction were respectively: 21·7, 43·2, and 97·4 minutes. What is the order of the reaction? (B.Sc. Hons., Manc.)

26. The transformation of γ-hydroxybutyric acid into its lactone is a reversible action of the first order, as represented by the equation—



$$CH_2OH.(CH_2)_2.CO_2H \rightleftharpoons CH_2-(CH_2)_2-CO+H_2O$$

Assuming that only the acid is present in a solution at the commencement of the reaction, show that the course of the reaction will be represented by the formula—

$$\frac{1}{t}\log\frac{A}{A-(1+a)x} = \text{const.}$$

where A is the concentration of the acid at the commencement of the reaction, x is the amount of lactone formed after the time t, and a is the ratio of the concentrations of the lactone and acid when equilibrium is attained.

Verify the formula for the following values of t and x, when A is 18·23 and a is 0·373.

t =	80	100	160
x =	7·08	8·11	10·35

(Inst. Chem. Phys., Jan., 1911.)

27. The concentrations of a compound undergoing complete change were 5·72, 3·23, 1·96, and at the times 10, 30, and 60 hours from the commencement of the reaction. Ascertain the apparent order of the reaction, the probable initial concentration of the compound, and the velocity constant.

(Hons., Manc., 1911.)

28. The rate of reaction between iodine and potassium phenyl propiolate in equivalent quantities was determined (James and Sudborough, *J.C.S.*, 1907, 1042) by measuring the rate of disappearance of the iodine. 25 c.c. of the solution was withdrawn after suitable intervals from the reaction mixture and titrated with $\frac{N}{10}$ sodium thiosulphate.

Time in hours.	Titration.
0	24·95
20	10·39
24	9·25
28	8·45
42	6·36

What is the order of the reaction, and what is the velocity constant?

29. When electrolytic gas was circulated over porcelain heated to 450° C. the following observations were made of the pressure of the gas remaining (dry) at intervals of 24 hours:—

Time, days	0	1	2	3	4	5
Pressure in mm. ...	465	232	116	58	29	14·5

What information do these figures afford as to the order of the change occurring? (B.Sc. Hons., Manc., 1907.)

30. In the reaction between equivalent quantities of potassium persulphate and hydrogen peroxide the rate of disappearance of the hydrogen peroxide was measured (Friend, *J.C.S.*, 1906, 1094). The numbers given below represent c.c. of $\frac{N}{50}$ potassium permanganate equivalent to the peroxide remaining in solution. What is the order of the reaction?

Time in hours.	C.c. of permanganate
0	14·06
1	13·19
2·5	12·05
3·5	11·35
5	10·36
7	9·16

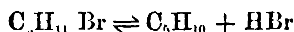
31. Potassium persulphate and potassium iodide interact with the liberation of iodine. 25 c.c. of a solution which was $\frac{1}{80}$ normal with respect to both the persulphate and iodide, were titrated from time to time with $\frac{1}{100}$ normal sodium thiosulphate. From the following results show that the reaction is bimolecular, t being the time of titration and x the number of c.c. of thiosulphate used.

t	9	16	32	50
x	4·52	7·80	14·19	20·05

(Inst. Chem. Phys., June, 1909.)

Equilibrium.

32. Amyl bromide dissociates according to the equation—



$$C_5H_{11}Br \rightleftharpoons C_5H_{10} + HBr$$

The density of amyl bromide vapour compared with air = 5·2 at temperatures up to 150° C. At 215° its density is 4·12 compared with air at the same temperature. Find the percentage dissociation at 215°.

33. The density of sulphur vapour varies gradually with the temperature, some of the values obtained being as follows:—

Temperature (° C.)	468	524	606	900–1100
Density (Air = ·1)	7·84	7·09	4·73	2·23

What information do these numbers give as to the nature of gaseous molecules of sulphur?

34. From the following numbers obtained by Natanson (*Wied. Ann.*, 1885, **24**, 465), for the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ at 21°, calculate for each pressure (i.) the percentage

dissociation of N_2O_4, (ii.) the partial pressures of N_2O_4 and NO_2 respectively, (iii.) the equilibrium constant.

Pressure (mm.)	43·58	101·64	230·6	492·1	617·6
Density (Air = 1)	2·049	2·283	2·501	2·684	2·722

The vapour density of NO_2 = 1·589. (Air = 1.)

35. If nitrogen peroxide is one-half dissociated under certain conditions, what proportion will remain undissociated when the volume is increased to ten times the original value while the temperature remains the same?

(Hons., Manc., 1910.)

36. In four experiments in which one gram-molecule of acetic acid was allowed to react with the following different quantities (x gram-molecules) of ethyl alcohol until equilibrium was established, Berthelot and Péan de Saint Gilles found that the following amounts of ethyl acetate (y gram-molecules) were produced:—

	(i.)	(ii.)	(iii.)	(iv.)
x	0·5	1·0	2·0	12·0
y	0·42	0·66	0·83	0·98

Show that these results are in accord with the law of Guldberg and Waage. (B.Sc. Hons., Vict., 1902.)

37. 1 litre of iodine vapour at 1092° and 760 mm. was found to weigh 2·25 grams. Calculate the proportion of monatomic molecules.

38. 2·447 grams of chloral hydrate dissolved in 100 grams of acetic acid lowered its freezing point 0·755°. Assuming K = 39 in the case of acetic acid, calculate the degree of dissociation of the chloral hydrate.

(B.Sc. Hons., Vict., 1903.)

39. Bodenstein (*Zeitschr. Physikal. Chem.*, 1897, **22**, 16) found that at 443° the dissociation of hydrogen iodide, according to the equation $2HI \rightleftharpoons H_2 + I_2$, was 21·98 per cent. For experiments at the same temperature starting with varying amounts of hydrogen and iodine, the amount of hydrogen iodide present when equilibrium was attained is given by the following numbers:—

Iodine (c.c. vapour). Initial.	Hydrogen (c.c.) Initial.	Hydrogen iodide (c.c.) Found.
2·94	8·10	5·66
5·30	7·94	9·52
9·27	8·07	13·34
14·44	8·12	14·82
27·53	8·02	15·40
33·10	7·89	15·12

Calculate from the first two columns, the amounts of hydrogen iodide predicted by the law of mass action, and compare them with the experimental numbers.

40. At 14° the distribution coefficient of iodine between carbon tetrachloride and water is 79. A solution of iodine in tenth-normal potassium iodide was shaken up with carbon tetrachloride. After equilibrium had been attained 1 litre of the carbon tetrachloride phase contained 0·02022 gram-molecule of iodine, whereas the same volume of the aqueous phase contained 0·02118 gram-molecule of iodine. Calculate the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$.

(Inst. Chem. Phys., January, 1911.)

41. The following data (Richardson, *J.C.S.*, 1887, **51**, 401) show the variation in density of nitrogen peroxide with change of temperature, produced by the dissociation $2NO_2 \rightleftharpoons 2NO + O_2$

Temperature.	Volume (corrected to N.T.P.).	Weight.
184° C.	143·5 c.c.	0·287 gram.
279° C.	116·6 „	0·226 „
494° C.	58·6 „	0·093 „
620° C.	19·6 „	0·027 „

What is the percentage of the total nitrogen peroxide which is dissociated at each temperature?

42. For the system $2CO \rightleftharpoons CO_2 + C$, the following results were found (Rhead and Wheeler, *J.C.S.*, 1910, **97**, 2178):—

	The equilibrium mixture contained	
Temperature.	Carbon dioxide.	Carbon monoxide.
850° C.	6·23 per cent.	93·77 per cent.
1000° C.	0·59 „	99·41 „
1200° C.	0·06 „	99 94 „

Calculate the constant in the expression—

$$\frac{19500}{T} + \log_e \frac{C^2_{CO}}{C_{CO_2}} = k$$

where T is the absolute temperature, C_{CO} and C_{CO_2} are the concentrations of carbon monoxide and carbon dioxide respectively.

Electrochemistry.

43. An electric current is passed simultaneously through the following solutions: hydrochloric acid, ferrous sulphate, ferric sulphate, and silver potassium cyanide. If 5·2 litres of hydrogen [at N.T.P.] were evolved from the hydrochloric acid solution, how much metal would be deposited in the case of the iron and silver salts? (Fe = 56, Ag = 108.) (B.Sc., Manc.)

44. An electric current is passed through a series of cells containing respectively acidified water, and aqueous solutions of common salt, copper sulphate, silver nitrate, and potassium acetate. What is the nature and amount of substance liberated in each cell if the current is allowed to pass until 50 c.c. [at N.T.P.] of oxygen have been liberated in the first cell? Na = 23, Cu = 63·5, Ag = 108, K = 39.

(Bd. of Ed., Stage III., Inorg., 1906.)

45. A current of electricity is passed through three cells in series. The first is provided with carbon electrodes, and the electrolyte is a 10 per cent. solution of hydrogen chloride. The second has a copper cathode and a carbon anode, and the electrolyte is a solution of copper sulphate slightly acidified with sulphuric acid. The third has a silver anode and a copper cathode, the electrolyte being a solution of silver nitrate, slightly acidified with nitric acid. State what reactions occur in each cell, and calculate the weight of the products at the anode and cathode of each cell per ampere-hour from the following data: one coulomb of electricity liberates 0·0000105 gram of hydrogen. (Inst. Chem., Min., July, 1910.)

46. Aluminium is manufactured by electrolysing a mixture of alumina, aluminium fluoride, and sodium fluoride. The

heat of combination of Al_2O_3 is 392 Cal., of AlF_3 is 249 Cal., of NaF is 102·6 Cal., all being stated in large calories per gram-molecule. Current is passed from one electrode to the other at a pressure of 6 volts. State what reactions occur and why; and calculate that fraction of the energy which is used in producing aluminium, and also state what use is made of the balance. (One large calorie = 4200 joules; one gram-equivalent requires 96,540 coulombs.)

(Inst. Chem., Min., March, 1909.)

47. A current which deposited 0·161 gram of silver in a silver voltameter was passed through a solution of silver nitrate. After the experiment the cathode liquid gave 1·6347 gram of AgCl and an equal volume of the solution before the experiment gave 1·7463 gram of AgCl. Calculate the transport numbers of the ions in the solution.

(2nd Year Hons. Class, Manc., 1909, adapted.)

48. From the electrolysis of hydrochloric acid in a cell with a cadmium anode the following results were obtained: Change in concentration of chlorine at anode and cathode respectively ± 0·00545 gram; silver deposited in voltameter connected in series with the cell, 0·0986 gram. Calculate the transport numbers of hydrogen and chlorine. (Cl = 35·46, Ag = 107·9.) (London Hons., Extl., 1909.)

49. A current which deposited 0·047 gram of copper in a voltameter containing copper sulphate, was passed through a solution of silver nitrate using silver electrodes. The liquid from the cathode contained, before the experiment, 1·315 gram of Ag, and after the experiment 1·231 gram of Ag. Calculate the transport numbers of the ions in the solution. (Ag = 107·9, Cu = 63·4.)

(2nd Year Hons. Class, Manc., 1911, adapted.)

50. A solution of potassium chlorate is electrolysed, and during electrolysis 0·3514 gram of silver is deposited in a silver voltameter in series. 41·079 grams of solution gave before electrolysis 1·0576 gram of potassium sulphate. The anode solution after electrolysis weighed 59·954 grams and gave 1·3802 gram of potassium sulphate. The anode was

cadmium, and was not attacked by chlorate ions. Find the transport number of the cation. (Inst. Chem., June, 1908.)

51. Calculate the transport number of the cation from the following experimental data:—

A current of 0·9 milliampere was passed through a $\frac{N}{100}$ solution of silver nitrate between silver electrodes for 6 hrs. 52 min. After the experiment 14·42 c.c. (the total anode solution) required 6·90 c.c. of $\frac{N}{25 \cdot 56}$ HCl for complete precipitation. (Electrochemical equiv. of silver = 0·001119.)

(Leeds Univ., Electrochem., 1905 adapted.)

52. Calculate the degree of ionisation in each of the following solutions of acetic acid; find also the dissociation constant of the acid. (Temp. = 25°.)

V (litres)	128	256	∞
Molec. conductivity	16·99	23·82	364

(Inst. Chem. Phys., Jan., 1911.)

53. A gram-molecular weight of an acid is contained in 30·15, 60·3, and 120·6 litres of solution respectively. The observed resistances for these concentrations are (i.) 92·9 ohms, (ii.) 135·4 ohms, (iii.) 200 ohms. The resistance of $\frac{N}{50}$ potassium chloride is 57 ohms in the same cell, and the molecular conductivity for potassium chloride of the same strength is 129·7. Calculate the value of K for each concentration. (μ_∞ for the acid is 350.)

(B.Sc. Hons., Vict., 1900.)

54. Calculate from the following data the volume of the solution which contains 1 gram-molecule of silver chloride at 13·8°: ratio of known resistance to that of the cell and contents, 1 : 53·02, the known resistance being 2140 ohms; limiting ionic conductivities of Ag and Cl respectively, 45·8 and 55·4; cell constant, *k*, 111·7.

(B.Sc. Hons., Lond., 1910.)

55. Given that the specific conductance of water at 18° is 0.038×10^{-6} mhos, and that the ionic conductivities at infinite dilution of hydrion and hydroxidion are 318 and 174 respectively, calculate the degree of ionisation of water.

(Inst. Chem. Phys., July, 1911.)

56. Calculate the percentage hydrolysis of sodium acetate in tenth-normal solution at 25° from the following data, assuming that the salt is completely dissociated:—

Dissociation constant of acetic acid = 0·000018
Ionic product for water = $1{\cdot}21 \times 10^{-14}$

(Inst. Chem. Phys., March, 1909.)

57. A 5 per cent. solution of cane sugar has a rotation of $\alpha_0 = +66{\cdot}7°$ in a 2-dm. tube. After complete inversion the rotation is $-19{\cdot}7°$. If the solution is 0·01 N with respect to hydrogen chloride, the angle of rotation decreases by 69·2° in 20 minutes. What is the velocity constant of inversion? What would be the value of the velocity constant if the hydrogen chloride were replaced by 0·1 N lactic acid, the dissociation constant of which is $1{\cdot}4 \times 10^{-4}$. The hydrogen chloride may be taken as completely dissociated in 0·01 N solution. [N.B.—*v* is in litres in dissociation formula.]

(Inst. Chem. Phys., Jan., 1910.)

58. The velocity constant of inversion of cane sugar by $\frac{N}{4}$ acetic acid at 25° is $0{\cdot}75 \times 10^{-3}$. Find the value of the constant when the acid solution is also $\frac{N}{40}$ with respect to sodium acetate, being given that the dissociation constant of acetic acid is 0·000018, and that the sodium acetate is dissociated to the extent of 86 per cent. [N.B.—*v* is in litres in dissociation formula.] (Inst. Chem. Phys., June, 1909.)

59. At a given temperature a litre of saturated silver bromate solution contains 0·0081 gram-molecules of salt; 0·0085 gram-molecules of silver nitrate are then added. Calculate the new solubility of the bromate, assuming both salts to be completely dissociated in solution.

(Inst. Chem., June, 1908.)

60. A lead accumulator with an electrolyte containing 1 gram-molecule H_2SO_4 per litre is joined in opposition to a similar cell with an electrolyte containing 0·01 gram-molecule acid per litre. Assuming all the acid to be dissociated, calculate the E.M.F. which will be given by the combination. (Use data in No. 61.) (Hons., Manc., Electrochem., 1911.)

61. A cell is arranged by having as one electrode a platinum plate surrounded by an atmosphere of hydrogen over a normal solution of an alkali (80 per cent. dissociated), and as the other electrode an atmosphere of hydrogen over a normal solution of acid (80 per cent. dissociated). Calculate the E.M.F. given by this cell, neglecting the P.D. at the boundary of the solutions, and state what change accompanies the discharge.

1 faraday = 96,540 coulombs. 1 joule = 0·24 cal.

conc. $H^{\cdot} \times$ conc. $OH' = 0{\cdot}56 \times 10^{-14}$ gram equivs. per litre

$\log_{10} x = 0{\cdot}4343 \log_e x$. $\log_{10} 1{\cdot}15 = 0{\cdot}060$.

(Hons., Manc., Electrochem., 1911.)

62. Calculate the E.M.F. of the Daniell cell, given that—



$$Zn + CuSO_4 = ZnSO_4 + Cu + 50{,}110 \text{ cals.}$$

1 volt-coulomb = 0·24 cal. 1 faraday = 96,540 coulombs.

Temp. coefficient = +0·000034 volts per degree.

(Hons., Manc., Electrochem , 1910.)

63. Find the E.M.F. of an oxyhydrogen cell from the following data :—



$$H_2 + O = H_2O + 67{,}520 \text{ cals.}$$

1 joule = 0·24 cal. 1 faraday = 96,540 coulombs.

Temp. coefficient of cell = − 0·0014 volts per degree.

(3rd Year Manc., 1910).

64. Calculate the heat of formation of lead chloride at 498° from the following data :—

The E.M.F. of the combination Cl_2/ molten $PbCl_2$/Pb is given by the formula, $e = 1{\cdot}263 - 0{\cdot}000679\ (t - 498)$ volts.

F = 96,540 coulombs. 1 joule = 0·2391 cal.

(Inst. Chem. Phys., March, 1909.)

Refractivities.

65. The value of $\frac{(n-1)}{d}$ for ethyl alcohol at 20° is 0·4528, for water at the same temperature 0·3324. The density of a mixture of alcohol and water at 20° was found to be 0·8558, and its refractive index 1·3616. Calculate the percentage of alcohol present. (Hons., Vict., 1899.)

66. Calculate the refractive power (using Gladstone and Dale's formula) of sodium chloride from the following data:—

22·2219 grams of an aqueous solution of sodium chloride contained 2·1336 grams of NaCl. The density of the solution at 19° was 1·06803 and its refractive index for sodium light was 1·34978. At the same temperature 1 gram of water occupies 1·001564 c.c. and has a refractive index of 1·33300. (Inst. Chem. Phys., Jan., 1910.)

Miscellaneous.

67. The vapour pressure of water at 99·8° is 754·58 mm., and at 100·2° it is 765·45 mm. Calculate the latent heat of vaporisation for 1 gram of water at 100°. Regnault's value for 100° is 537 calories; how do you account for the difference between the calculated and experimental values?

(Inst. Chem. Phys., July, 1910.)

68. If the ignition temperature of electrolytic gas is 585°, what adiabatic compression would cause ignition, if the gas were originally at 15° C. and 1 atmosphere pressure? Assume for the purpose of this calculation that the ignition temperature is not altered by variation of pressure. ($\gamma = 1·41$.)

(For this and the following calculation, compare K. G. Falk, *J. Amer. Chem. Soc.*, 1906, **28**, 1517; 1907, **29**, 1536; and H. B. Dixon, Presidential Address to the London Chemical Society, *J.C.S.*, 1910 and 1911.)

69. A column of gas of composition represented by $H_2 + 3O_2$ and of length 540 mm. was compressed adiabatically into a length of 40 mm. without ignition; into a length of 36 mm. with ignition resulting. The cross-section of the

column being constant, show that the ignition temperature of the mixture (at the pressure of the experiment) lies between 550° and 578°. Assume γ (ratio of the specific heats at constant pressure and constant volume) = 1·40, and the initial temperature of the gases 17·5 and 15° respectively.

(H. B. Dixon, *Jour. Chem. Soc.*, 1911, 99, 590.)

70. Calculate the approximate molecular heat of solution of aniline (C_6H_7N) in water, given the following data:—

1 part by weight of aniline dissolves in 31·5 parts by weight of water at 12·5° and in 32·1 parts at 16°.

$\log_{10} 3{\cdot}15 = 0{\cdot}4983.$ $\log_{10} 3{\cdot}21 = 0{\cdot}5065.$

$$\log_e x = 2{\cdot}303 \log_{10} x.$$

(Hons., Manc., 1911.)

71. The melting point of acetic acid is 16·6° C.; its heat of fusion is 46·42 calories; and the value of $\frac{dT}{dp} = 0{\cdot}0242°$. Calculate the change in volume when 1 gram of solid acetic acid is melted. (London Hons., Intl., 1908.)

72. The mean distance between two nodes for a tube filled with dry CO_2 was found to be 4·528 cm., when filled with dry air under the same conditions the distance was found to be 5·948 cm. If the ratio $\frac{C_p}{C_v}$ for air is 1·41 and its density is 14·45, calculate the ratio $\frac{C_p}{C_v}$ for CO_2.

(B.Sc. Hons., Manc.)

73. The vapour pressure of a substance varies with temperature according to the equation—

$$\log p = a - \frac{b}{T}$$

where p is the vapour pressure, T the absolute temperature, and a and b constants, b being connected with the heat of reaction per gram-molecule of gas produced (q), by the equation—

$$q = \log_e 10 \, . \, Rb$$

R being the gas constant ($\log_e 10 = 2{\cdot}30$).

Caven and Sand (*J.C.S.*, 1911, 1359) found the following relations for sodium carbonate monohydrate:—

$$\log p = 10{\cdot}825 - \frac{3000{\cdot}0}{T}$$

and for sodium bicarbonate ($2NaHCO_3$)—

$$\log p = 11{\cdot}8185 - \frac{3340{\cdot}0}{T}$$

Calculate q in each of these cases and compare the second value with that obtained from the following thermochemical data:—

$$[Na, H, C, O_3] = 228{,}380 \text{ cal.}$$
$$[Na_2, C, O_3] = 271{,}970 \text{ ,,}$$
$$[H_2, O] = 58{,}060 \text{ ,,}$$
$$[C, O_2] = 97{,}000 \text{ ,,}$$

ANSWERS

CHAPTER II

1. 1 silver : 0·149 sulphur in each case (Berzelius).

1 silver :	0·14852	sulphur	(Stas)
„	0·14854	„	
„	0·14854	„	
„	0·14851	„	
„	0·14849	„	

2. 1 silver : 0·32841 chlorine.

„	0·32844	„
„	0·32843	„
„	0·32850	„
„	0·32846	„
„	0·32848	„
„	0·32842	„

3. 39·1620
39·1605
39·1560
39·1527
39·1550
39·150
39·147
39·156

4. Lead ... 74·62 per cent
Chlorine 25·46 „
100·08

5. Ratio of nitrogen in (i.) to nitrogen in (ii.), combined with the same weight of oxygen is 2·000.

6. 1st contains 3·0 A to 1·0 B.
2nd „ 4·0 A to 1·0 B.
3rd „ 6·00 A to 1·00 B.

7. Ratio of arsenic in A to arsenic in B combined with same weight of iron is 2·66 : 1·35 = 2 (approx.).

8. Ratio of sulphur in A to sulphur in B combined with same weight of oxygen is 1 : 1·497 = 2 : 3 (approx.).

Ratio of iron in A to iron in B combined with same weight of oxygen is 1 : 1·499 = 2 : 3 (approx.).

Ratio of carbon in A to carbon in B combined with same weight of oxygen is 1 : 2·000.

9. Ratio of copper oxide in copper sulphate to copper oxide in basic sulphate combined with the same weight of sulphuric anhydride is 1·04 : 4·00 = 1 : 4 (approx.).

10. Ratio of iron in first compound to iron in pyrites combined with the same weight of sulphur is 1·99 : 1 = 2 : 1 (approx.).

11. Ratio of copper in black oxide to copper in other oxide combined with the same weight of oxygen is 1 : 2·00.

12. $\frac{\text{Iodine}}{\text{Potassium}} = 3{\cdot}58$ (from potassium iodide).

$\frac{\text{Iodine}}{\text{Potassium}}$ (combined with same weight of chlorine) = 3·58.

13. 1 gram of hydrogen combines with 3·00 or 6·00 grams of carbon, either of which quantities will combine with 8·00 grams of oxygen, which in turn combines directly with 1 gram of hydrogen.

14. Sulphur, 39·9.
Oxygen, 60·1.

15. 12·1. **16.** 108. **17.** 107·9. **18.** 10·34 ± 0·02.

19. 7·94; 1·00; 31·57; 15·89; 35·17. **20.** 32·0; 64·2.

CHAPTER III

1. 34·0 c.c., 340 c.c. **2.** 444 mm. **3.** 3·0 atmospheres.

4. 22·78 c.c., 9·18 c.c., 0·45 c.c. **5.** 65·5 c.c. **6.** 10 c.c.

7. 265 c.c., 322 c.c., 449 c.c., 549 c.c. **8.** The former.

9. 240° C. **10.** The former. **11.** 273 c.c.

12. 0·67 atmosphere. **13.** The former.

14. { 9·2 mm. water vapour.
370·5 mm. oxygen.
370·5 mm. nitrogen. }

15. 150 c.c. 16. 15·0 c.c.

17. { Oxygen, 20·5 per cent.
Water vapour, 2·0 per cent.
Nitrogen, 77·5 per cent. }

18. 731 mm. total : 542 mm. hydrogen, 77 mm. oxygen, 112 mm. nitrogen.

CHAPTER IV

1. 249·76 grams. 2. 99·404 c.c.
3. 1·0519, 1·0525, 1·05273, 1·0514, 1·05157, 1·0517.
4. 65 c.c.
5. 0·0046 gram, 0·0043 gram. 6. 134·873 grams.
7. 2·19 ± 0·03, 2·14 ± 0·03, 2·17 ± 0·04. 8. 2·02 grams.
9. 140° C. 10. 126. 11. 96·7. 12. 38·7. 13. 37·8.
14. 52·0. 15. 75.
16. 46, 23, 15·3. $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$.
18. 12.

CHAPTER V

1. 65·4. 2. 29·5, 118·0. 3. 8·67, 52·0. Hexavalent.

4. $M_2O(80)$, $MO(80)$, $M_2O_3(240)$, $MO_2(160)$. Accept 80, *i.e.* MO (atomic weight of metal 64). 5. 26·6, MCl_3.

6. 29·7, 119. 7. 58·6. 8. 519 c.c.

9. 214, which is molecular weight of $GeCl_4$.

10. 3·67, 11·0. 11. 11·04, 10·95. 12. 197·3.

13. 107·89, 107·93.

14. 127·55, 127·55, 127·53, 127·53, 127·53. 15. 35·41.

16. 35·48. 17. 12·00, 12·06. 18. 48·1. 19. 39·8.

20. 200·1. Molecular wt. approx. 198, *i.e.* mercury vapour is monatomic, and its exact molecular wt. is 200·1.

21. 1·006; or if CO_2 is absorbed by potash in drying tubes, 1·008. 22. 18·017 grams. 1·009.

CHAPTER VI

1. K, 56·6; C, 8·7; O, 34·7. **2.** H, 5·93; O, 94·07.
3. Fe, 34·42; O, 65·58.
4. N, 21·40; O, 24·44; Cl, 54·16.
5. Na, 32·8; Al, 12·9; F, 54·3.
6. N, 6·31; H, 1·82; Pt, 43·96; Cl 47·91.
7. C, 31·98; H, 6·72; N, 18·67; O, 42·64.
8. C, 55·35; H, 7·75; O, 36·90.
9. C, 39·98; H, 2·80; O, 26·65; S, 17·81; Na, 12·77.
10. CuO, 71·96; CO_2, 19·90; H_2O, 8·15.
11. Al_2O_3, 39·5; SiO_2, 46·6; H_2O, (const.) 7·0; H_2O, (hyd.) 7·0. **12.** H_2O, 62·96; Na_2CO_3, 37·04.
13. K, 17·2; Na, 5·1; Co, 13·0; NO_2, 60·8; H_2O, 3·9.
14. 29·2 per cent. gold from analysis and from formula.
15. $(C_8H_{15}O_3)_2Ba$; (30·15 per cent. Ba). $(C_8H_{15}O_3)_2Ba$ requires 30·42 per cent. **16.** FeO. **17.** $C_{10}H_8$.
18. Na_3AlF_6. **19.** $NiCO_3$, K_2CO_3, $4H_2O$.
20. $CuSN_2O_5H_8$. ($CuSO_4$, $2NH_3$, H_2O.)
21. 3BeO, Al_2O_3, $6SiO_2$. **22.** 0·209 gram.
23. CaO, Al_2O_3, $6SiO_2$, $6H_2O$.
24. $Th(NH_4)_4(C_2O_4)_4 7H_2O$.
25. $Pb(NO_3)$ (FeC_6N_6), $5H_2O$.
26. $K_4Cr_2(C_2O_4)_4(OH)_2$ or $K_2Cr(C_2O_4)_2OH$.
27. $2K_2S_5O_6$, $3H_2O$. **28.** $Hg(NO_2)_2$, $3KNO_2$, H_2O.
29. 28·0. **30.** $[Fe, Al]_2O_3$, [Fe, Mg]O.
31. $[Ni, Fe, Mg]_3(AsO_4)_2$, $8H_2O$.
32. Na_2O, Al_2O_3, $3SiO_2$, $2H_2O$.
33. $FeWO_4$, or [Fe, Mn, Ca, Mg] WO_4.
34. $2CaO.2SiO_2.[Al, B]_2O_3.H_2O$, or $Ca[Al, B]OH.SiO_4$.
35. $3Al_2O_3.3Na_2O.6SiO_2.2NaCl$.
36. $ZnP_2O_3Cl_6$. **37.** $Ca_2Si[O, F_2]_4$.

CHAPTER VII

1. 94·5 grams. **2.** 6·1 grams of KCl, 3·9 grams of oxygen, 5·6 grams of CaO, 4·4 grams of CO_2. **3.** 74·6 lbs.
4. 296 grams per litre. **5.** 6·004 in CO, 3·002 in CO_2.

6. 8·09 grams, 7·67 grams. **7.** 48·0 per cent.

8. 29 per cent. **9.** 63·0.

10. M_3O_4, MO_2. Atomic weight of metal calculated from nitrate or either oxide is 207.

11. 29·4 per cent. FeO. 70·6 per cent. Fe_2O_3.

12. 43·7. **13.** 103·5, 207.

14. $3TlCl + 2AuBr_3 = 2Au + TlCl_3 + 2TlBr_3$.

15. $K_2Cr_2O_7 + 6Hg + 14HCl = 2CrCl_3 + 3Hg_2Cl_2 + 2KCl + 7H_2O$. **16.** 2·9 per cent.

17. 60·0 per cent. KCl, 30·0 per cent. KBr, 10·0 per cent. KI.

18. Add 11·3 grains NaOH and 1·1 grains Na_2CO_3 per gallon. (Ca is precipitated as $CaCO_3$, Mg as $Mg(OH)_2$.)

19. 8·16 grams, 29·19 grams. **20.** 38 grams, 158 grams.

21. 0·933 gram. **22.** 89·41 per cent.

23. 2·54 grams (if the gases remain in contact with the solution for some minutes). **24.** 0·200 gram. **25.** 800 lbs.

26. KI 0·313 gram. NaCl 0·687 gram.

27. KCl 73·8 per cent. KI 26·2 per cent.

28. $CaSO_4$ 43·2 per cent. $CaCO_3$ 56·8 per cent.

29. NaCl 42·5 per cent. KCl 57·5 per cent.

30. BaO 81·4 per cent. BaO_2 18·6 per cent. (*a*) 11·8, (*b*) 1·2.

31. 0·0198 gram, 0·432 gram, 0·295 gram, 0·432 gram.

32. 11·1 litres, 0·509 litre, 0·746 litre, 0·509 litre.

33. 274 c.c., 16·3 c.c., 110 c.c. **34.** 0·226 gram.

35. 4·00 grams, 267 c.c.

36. 18·7 litres of hydrogen, 9·3 litres of oxygen.

37. 33·3 grams, 11·4 litres. **38.** 497 grams, 662 grams.

39. 209 c.c. **40.** (*a*) 16·3 c.c., (*b*) 32·6 c.c., (*c*) 16·3 c.c.

41. 5·6 litres in each case. **42.** 630 mm.

43. 0·47 gram Na. 1·20 grams NaCl.

44. 43·9 grams. 16·8 litres.

45. 367 grams, 3800 litres. **46.** 18·7 litres.

47. 22·4 litres, 22·4 litres, 11·2 litres.

48. 35·5 grams, 8·7 litres.

49. 30 grains S per 100 cu. ft. 0·69 mgr. S per litre 0·48 c.c. H_2S per litre. **50.** 33·5 kilos. of sulphur.

51. 6·32 grams per litre.

52. 131·0 grams, 120·1 grams, 322 c.c.

53. 58·6 per cent., 670 c.c., 720 c.c.

54. 5·6 litres (assuming no SO_3 formed). 14·9 litres.

55. H_2S : 10·6 grams, 7·0 litres. SO_2 : 20·0 grams, 7·0 litres.

56. 35·2 litres. **57.** 27·5 litres. **58.** 95·1 per cent.

59. H_2S. **60.** 2·43 litres at N.T.P. 37·0 grams.

61. 61 per cent. $CaCO_3$. 39 per cent. $MgCO_3$.

62. 3 : 2.

63. 90 cubic metres air. 10·5 kilograms water. 12·4 cubic metres CO_2.

64. 155 thousand cubic feet.

CHAPTER VIII

1. 20 c.c. CO. **2.** 5·0 litres oxygen ; 10·8 litres CO_2.

3. 22·4 litres. **4.** 456 litres.

5. (*a*) Production of SO_2 involves no change in volume, but the small amount of SO_3 produced in such a combustion would cause a corresponding small contraction.

(*b*) 20 c.c. contraction.

(*c*) Total contraction on 3 litres of 1 litre, or resultant volume is 2 litres.

6. 29·8 litres. **7.** 68 grams ; 4·8 litres.

8. 60 vols. CO_2 ; 55 vols. oxygen.

9. 60 vols. CO_2 ; 44 vols. oxygen.

10. CO_2, 807 c.c. ; H_2O, 1571 c.c. ; SO_2, 2·7 c.c. ; N_2, 5554 c.c.

11. 44·8 litres ; 104 litres. **12.** 327° C.

13. 2·0027 vols.

14. 2·005 vols. hydrogen : 1 vol. oxygen ; Density = 5·96.

15. ClO_2. 60 c.c. **16.** NO. **17.** C_2H_2.

18. C_3O_2.

19. 79 vols. nitrogen ; 38 vols. hydrogen assuming the original gases to be measured saturated with water vapour.

20. 36 c.c. oxygen ; 64 c.c. nitrogen.

21. 90 c.c. CO; 10 c.c. CH_4.

22. 40 vols. oxygen; 40 vols. N_2O; 20 vols. nitrogen.

23. 38·2 per cent. N_2O; 49·4 per cent. NO; 12·4 per cent. nitrogen. **24.** 60 vols. CO; 40 vols. acetylene.

25. 30 c.c. CS_2; 70 c.c. C_2N_2.

26. 2 c.c. C_2H_2; 6 c.c. hydrogen; 12 c.c. CO.

27. 12·5 per cent. hydrogen; 7·5 per cent. CH_4; 80·0 per cent. nitrogen. **28.** 22·4 per cent.

29. 12·6 per cent., C_2H_4; 41·9 per cent. CO; 43·6 per cent hydrogen; 1·9 per cent. nitrogen.

30. 0·28 per cent. CO_2; 1·22 per cent. CH_4.

31. CO_2, 1·3; CO, 48·0; C_2H_4, 2·7; CH_4, 2·3; hydrogen, 43·4; nitrogen, 2·3 per cent.

32. CO_2, 0·7; C_2H_4, etc., 4·2; CO, 7·0; CH_4, 40·0; hydrogen, 48·0 per cent.

33. CH_4, 38·6 c.c.; C_2H_6, 9·0 c.c.; nitrogen, 5·9 c.c.

34. CO, 4 c.c.; CH_4, 4 c.c.; C_2H_6, 2 c.c.

35. CS_2, 40 c.c.; CO, 20 c.c.; 10 per cent.

36. CH_4, 0·43 per cent.; nitrogen, 0·04 per cent.

37. CO_2, 64·7 per cent.; N_2O, 20·5 per cent.; CO, 6·3 per cent.; nitrogen, 8·5 per cent.

38. Oxygen, 17·65 c.c.; ozone, 18·59 c.c.; CO, 39·96 c.c.; CO_2, 9·67 c.c.

39. (*a*) Possible. (*b*) Impossible. No.

CHAPTER IX

1. 4·815 grams. **2.** 4·00 grams; 2·36 litres.

3. 3·54 grams in 100 c.c.; 3·50 grams in 100 grams; 6·62 c.c. **4.** 3·95 grams; 5·64 grams.

5. 11·2 c.c. gaseous SO_2 at N.T.P. **6.** 97·5 per cent.

7. SO_3, 66·6; H_2SO_4, 33·4 per cent.

8. 0·451 gram sodium as hydroxide.
0·038 ,, ,, ,, peroxide.

9. 77·7 per cent.; 92·8 per cent. **10.** NOCl.

11. (*a*) 74 per cent. (*b*) 26 per cent.

CHAPTER X

1. CH_4O. 2. CH_2O. 3. C_2H_6O.

4. $C_3H_6O_2$. 5. C_2H_4O.

6. C_3H_8O. (Propyl alcohol, isopropyl alcohol, methyl ethyl ether.)

7. $C_{16}H_{11}O_3Br$. 8. $C_4H_7O_2Br$. 9. $C_2H_2O_4$; oxalic acid.

10. $C_4H_{11}N$.[$CH_3.CH_2.CH_2.CH_2.NH_2$; $(CH_3)_2.CH.CH_2.NH_2$; $(CH_3)_3.C.NH_2$; $\begin{matrix} CH_3.CH_2 \\ CH_3 \end{matrix} \rangle CH.NH_2$; $(C_2H_5)_2NH$;
$\begin{matrix} CH_3.CH_2CH_2 \\ CH_3 \end{matrix} \rangle NH$; $\begin{matrix} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle CH \\ CH_3 \end{matrix} \rangle NH$; $\begin{matrix} C_2H_5 \\ CH_3 \\ CH_3 \end{matrix} \rangle N$]

11. $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \rangle C:N.OH$ from methyl ethyl ketone.

12. $C_9H_8O_3Br_2$.

13. Empirical formula CH_2Cl.

$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \quad \text{and} \quad \begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix}$$

14. $CH_3.CO.NH_2$, acetamide.

15. $\begin{matrix} CHOH.COOH \\ | \\ CH_2.COOH \end{matrix}$ malic acid.

$CH_3.C(OH).(COOH)_2$ isomalic acid.

$CH_2OH.CH.(COOH)_2$ β-hydroxy isosuccinic acid.

16. $C_6H_5.CH_3$.

17. C_6H_{10}. A doubly unsaturated aliphatic hydrocarbon.

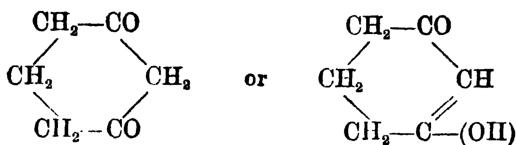
18. CHO_2; $C_2H_2O_4$. 19. C_7H_9N.

20. CH_3O_3. The compound is $(COOH)_22H_2O$.

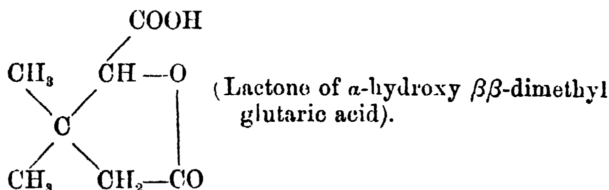
21. *o*-xylene $C_6H_4(CH_3)_2$.

22. The simplest formula is C_3H_4O, but the bromine compound is $C_6H_7BrO_2$. Hence A is $C_6H_8O_2$. With alcohol and sulphuric acid it gave $C_6H_7(C_2H_5)O_2$, thus indicating the presence of a hydroxyl group. Hydroxylamine gave a dioxime, indicating two ketonic groups. Hence, since there are only

two atoms of oxygen in A, one group—$CH_2.CO$—must exist and behave both as a ketone and as—$CH = C(OH)$—. Dihydroresorcinol satisfies all the conditions. Its formula is represented as—



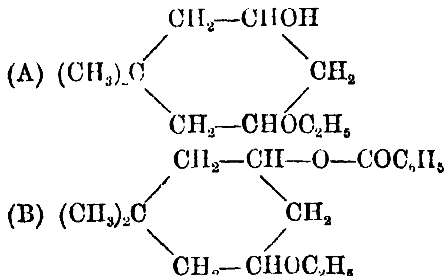
23.



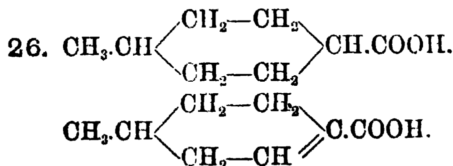
(Lactone of α-hydroxy ββ-dimethyl glutaric acid).

24. Salt is $C_6H_{17}O_7N_3$ and acid $C_6H_8O_7$, or $C_3H_5O(COOH)_3$, *i.e.* citric acid or an isomer.

25.



26.



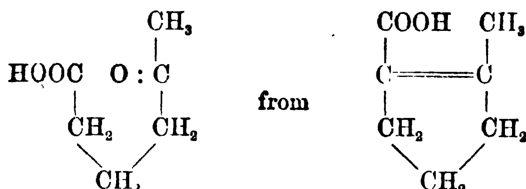
27. *αα*-dimethyl glutaconic acid,



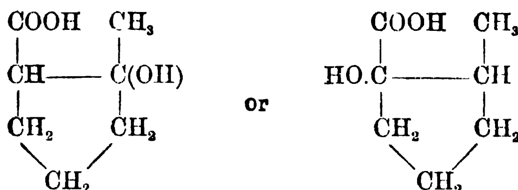
$COOH.C(CH_3)_2.CH:CH.(COOH)$.

28. $C_7H_{12}O_3$ or $C_6H_{11}O(COOH)$. A number of isomeric keto and aldehyde heptylic acids have the above formula.

29. γ-aceto butyric acid is $C_6H_{10}O_3$. This is formed by oxidation of an acid $C_7H_{10}O_2$ thus:—

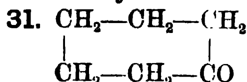


The cyclic hydroxy-monobasic acid is then either



Alternatively, the carboxyl group may be exchanged in the last three formulæ for one of the hydrogen atoms in a CH_2 group.

30. The first two acids are represented by the molecular formulæ $C_9H_{16}O_2$ and $C_9H_{14}O_2$. *m*-xylene being C_8H_{10}, the third acid must be monocarboxylic, *i.e.* $C_9H_{10}O_2$, a dimethyl benzoic acid. The first and second are then hexa-hydro and tetra-hydro-dimethyl benzoic acids.

31. 

CHAPTER XI

1. + 21,485 cal. **2.** + 18,550 cal. **3.** + 33,740 cal.

4. CH_4 : + 21,750.
C_2H_6: + 28,560.
C_2H_4: − 2710.
C_2H_2: − 47,779.
C_6H_6: − 12,510.

5. + 27·7 Calories. **6.** + 53,000 cals.

7. + 99,420 cals.
8. (i.) + 48·7 Cals. (ii.) + 55·2 Cals.
9. + 131·0 Cal. **10.** + 97,689 cal.
11. [Fe, Cl_2] = + 82,048 cal. [Fe, Cl_2] = + 96,038 cal.
12. [H, Cl] = + 22,000 cals.
[H, I] = − 6100 cals.
13. + 1055·5 k.
14. A. 29,973. B. 29,895.
15. + 26,707. + 11,889. **16.** 192,700 cal.
17. 11,520 cals. **18.** 4503 cals. 8105 B.T.U.
19. C_2H_6. 371,600 cals.
20. 63,639. 71,339. 142,419. 103,249.
21. 369,000. 332,198. 309,195.
22. 801·6 Cal. **23.** 40·2 kgr. cent. units.
24. 25,000 cub. ft. **25.** 3660°. 1950°.
26. 10,180°. 2755°.

CHAPTER XII

1. 1 volume nitrogen with 3·003 volumes hydrogen, in each case. N = 14·01 (H = 1·008). The data do not permit a distinction to be drawn.

2. 71·2 atmospheres. − 93° C.

3. 15 minutes. **4.** 279 seconds.

5. The density of nitrogen, by comparison of its rate of diffusion with that of (*a*) hydrogen, is 14·1, (*b*) oxygen, is 14·3.

6. (*a*) 0·703. (*b*) 24·7. (Atomic weights used: Cl = 35·46, H = 1·008.)

7. 82. **8.** 20.

9. 32 per cent. oxygen, 61 per cent. nitrogen, 7 per cent. CO_2.

10. 20·7 per cent. oxygen, 78·4 per cent. nitrogen, 0·9 per cent. CO_2.

11. 365 mm. oxygen, 136 mm. CO_2. Total = 501 mm.

12. 196 mm. nitrogen, 564 mm. NO. From 1 volume of the mixed gases, 0·939 volume remains unabsorbed.

13. 50 cm. mercury. **14.** 0·30 atmosphere. **15.** 30·6.
16. 315. **17.** $H^{\cdot} + H^{\cdot} + Cr_2O_7''$. **18.** 60. **19.** 113.
20. 1700 calories per gram-atom.

21. Molecular weight from first two determinations = 164, from last two = 144. The molecular weight of formic acid is 46.

22.  $C_{20}H_{28}N_2O_5$.

23. $\frac{1}{t}\log_{10}\frac{C_o}{C_t}$ = 0·0309, 0·0332, 0·0350, 0·0370, 0·0365, 0·0322, 0·0323, 0·0340, 0·0267.

24. $\frac{1}{t}\log_{10}\frac{C_o}{C_t}$ = 0·00564, 0·00631, 0·00598.

25. Second **26.** Const. = 0·00414, 0·00410, 0·00410.

27. Second order.
Initial concentration (mean) = 9·26.
Velocity constant (mean) = 0·00670.

28. Second. $2{\cdot}81 \times 10^{-3}$, $2{\cdot}83 \times 10^{-3}$, $2{\cdot}80 \times 10^{-3}$, $2{\cdot}79 \times 10^{-3}$.

29. The numbers would be regarded as proving the reaction to be monomolecular, were it to be proceeding in a homogeneous system. Since it is taking place on the surface of the porcelain, no deduction can be made as to the order of the reaction. (See Bone and Wheeler, *Phil. Trans.*, 1906.)

30. First. **31.** 0·000255, 0·000259, 0·000257, 0·000253.

32. 26·2 per cent.

33. Over the range 900°–1100° the molecules are S_2; as the temperature falls, a greater proportion of more complicated molecules is formed, until the density approaches, but does not reach that corresponding with S_8.

34.

Per cent. diss.		55·09, 39·20, 27·07, 18·40, 16·75
Partial press.	N_2O_4	12·62, 44·39, 132·4, 339·1, 440·4
	NO_2	30·96, 57·25, 98·2, 153·0, 177·2
$K = \frac{C^2_{NO_2}}{C_{N_2O_4}}$		75·9, 73·8, 72·9, 69·0, 71·3.

35. **14·6 per cent.**

36. $K = \frac{C_{ester} \cdot C_{water}}{C_{acid} \cdot C_{alcohol}}$ = (i.) 3·8, (ii.) 3·8, (iii.) 3·5, (iv.) 4·4.

37. 1·5 per cent. of total number of molecules are monatomic. **38.** 31 per cent.

39. 5·64, 9·49, 13·47, 14·93, 15·54, 15·40.

40. $\frac{C_{KI} \cdot C_{I_2}}{C_{KI_3}} = 0{\cdot}000967.$

41. 5 per cent., 12 per cent., 59 per cent., 98 per cent.

42. 20·01, 20·44, 20·65.

43. Iron 13·0, 8·7 grams; silver 50·1 grams.

44.

	Negative Pole.	Positive Pole.
First cell.	100 c.c. hydrogen.	50 c.c. oxygen.
Second cell.	100 c.c. hydrogen. 0·358 gr. NaOH	100 c.c. chlorine (less amount dissolved).
Third cell.	0·283 gr. copper.	50 c.c. oxygen. 0·438 gr. H_2SO_4.
Fourth cell.	0·964 gr. silver.	0·563 gr. HNO_3. 50 c.c. oxygen.
Fifth cell.	100 c.c. hydrogen. 0·500 gr. KOH.	100 c.c. C_2H_6. 200 c.c. CO_2.

45.

	Cathode.	Anode.
First cell.	0·0378 gr. hydrogen.	1·330 gr. chlorine.
Second cell.	1·192 gr. copper.	0·300 gr. oxygen. 1·840 gr. H_2SO_4.
Third cell.	4·047 gr. silver.	6·373 gr. $AgNO_3$.

46. 47·4 per cent. **47.** Ag : 0·478. NO_3 : 0·522.

48. H : 0·832. Cl : 0·168.

49. Ag : 0·475. NO_3 : 0·525.

50. 0·574. **51.** 0·455.

52. 0·0467, 0·0654. $1{\cdot}79 \times 10^{-8}$ (v in c.c.).

53. $72{\cdot}3 \times 10^{-8}$, $72{\cdot}3 \times 10^{-8}$, $72{\cdot}2 \times 10^{-8}$ (v in c.c.).

54. 103,000 litres.

55. $0{\cdot}77 \times 10^{-7}$ gram-molecule per litre.

56. 0·0082 per cent. **57.** 0·0350, 0·0129.

58. $0{\cdot}067 \times 10^{-8}$. **59.** 0·0049 gram-molecule per litre

60. $0{\cdot}109 + 0{\cdot}0004t$. **61.** $0{\cdot}76 + 0{\cdot}0028t$.

62. $1{\cdot}090 + 0{\cdot}000034t$. **63.** $1{\cdot}075 - 0{\cdot}0014t$.

64. 82·5 Cal. **65.** 74·8. **66.** 0·2708.

67. 547 calories. It is assumed that steam behaves as a perfect gas; its volume is, however, less than that calculated, hence the difference.

68. 43 atmospheres

70. 890 calories

71. + 0·161 c.c.

72. 1·24.

73. 13,800 calories.
30,700 calories.
29,700 calories.

SOME CONVERSION NUMBERS

The student will remember the following after using them for a short time. He will find them sufficient to enable him to perform most of the conversions he may meet.

Length.

1 metre = 39·37 inches. 1 inch = 2·54 cm.

Mass.

1 gram = 15·43 grains. 1 ounce (avoirdupois) = 28·35 grams.

Volume and Mass.

1 gallon of water (at 62° F.) = 10 lbs. avoirdupois = 70,000 grains.

1 litre of hydrogen at N.T.P. weighs 0·0899 (or 0·09) gram.

1 litre of air at N.T.P. weighs 1·293 gram.

The gram-molecular weight of a gas occupies at N.T.P. approximately 22·4 litres.

Temperature.

t° C. = $(\frac{9}{5}t + 32)^\circ$ F.

Specific Gravity.

$$\text{Specific gravity} = \frac{5 \times \text{Twaddell reading} + 1000}{1000}$$

Logarithms.

$\text{Log}_e\, a = \log_{10} a \times 2{\cdot}3026.$ $\text{Log}_{10}\, a = \log_e a \times 0{\cdot}4343.$

VAPOUR PRESSURE OF WATER

°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.
0	4·6	10	9·2	20	17·4	30	31·6
1	4·9	11	9·8	21	18·5	40	55·0
2	5·3	12	10·5	22	19·7	50	92·2
3	5·7	13	11·2	23	20·9	60	149·2
4	6·1	14	11·9	24	22·2	70	233·8
5	6·5	15	12·7	25	23·5	80	355·5
6	7·0	16	13·6	26	25·0	90	526·0
7	7·5	17	14·5	27	26·5	100	760·0
8	8·0	18	15·4	28	28·1		
9	8·6	19	16·4	29	29·8		

DENSITY OF WATER

0°	0·99987	18°	0·99862
1°	93	19°	43
2°	97	20°	23
3°	99	21°	02
4°	1·00000	22°	0·99780
5°	0·99999	23°	56
6°	97	24°	32
7°	93	25°	07
8°	88	26°	0·99681
9°	81	27°	54
10°	73	28°	26
11°	63	29°	0·99597
12°	52	30°	67
13°	40	31°	37
14°	27	32°	05
15°	13	33°	0·99473
16°	0·99897	34°	40
17°	80	35°	06

1912.

		O = 16.			O = 16.
Aluminium ...	Al	27·1	Neodymium ...	Nd	144·3
Antimony ...	Sb	120·2	Neon	Ne	20·2
Argon	A	39·88	Nickel	Ni	58·68
Arsenic	As	74·96	Niton (radium emanation) ...	Nt	222·4
Barium	Ba	137·37	Nitrogen ...	N	14·01
Bismuth ...	Bi	208·0	Osmium ...	Os	190·9
Boron	B	11·0	Oxygen ...	O	16·00
Bromine ...	Br	79·92	Palladium ...	Pd	106·7
Cadmium ...	Cd	112·40	Phosphorus ...	P	31·04
Cæsium	Cs	132·81	Platinum ...	Pt	195·2
Calcium ...	Ca	40·07	Potassium ...	K	39·10
Carbon	C	12·00	Praseodymium ...	Pr	140·6
Cerium	Ce	140·25	Radium ...	Ra	226·4
Chlorine ...	Cl	35·46	Rhodium ...	Rh	102·9
Chromium ...	Cr	52·0	Rubidium ...	Rb	85·45
Cobalt	Co	58·97	Ruthenium ...	Ru	101·7
Columbium ...	Cb	93·5	Samarium ...	Sa	150·4
Copper	Cu	63·57	Scandium ...	Sc	44·1
Dysprosium ...	Dy	162·5	Selenium ...	Se	79·2
Erbium ...	Er	167·7	Silicon	Si	28·3
Europium ...	Eu	152·0	Silver	Ag	107·88
Fluorine ...	F	19·0	Sodium	Na	23·00
Gadolinium ...	Gd	157·3	Strontium ...	Sr	87·63
Gallium ...	Ga	69·9	Sulphur	S	32·07
Germanium ...	Ge	72·5	Tantalum ...	Ta	181·5
Glucinum ...	Gl	9·1	Tellurium ...	Te	127·5
Gold	Au	197·2	Terbium ...	Tb	159·2
Helium	He	3·99	Thallium ...	Tl	204·0
Hydrogen ...	H	1·008	Thorium ...	Th	232·4
Indium	In	114·8	Thulium ...	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium ..	Ti	48·1
Iron	Fe	55·84	Tungsten ..	W	184·0
Krypton ...	Kr	82·92	Uranium ...	U	238·5
Lanthanum ...	La	139·0	Vanadium ...	V	51·0
Lead	Pb	207·10	Xenon	Xe	130·2
Lithium ...	Li	6·94	Ytterbium (Neoytterbium) ...	Yb	172·0
Lutecium ...	Lu	174·0	Yttrium ...	Yt	89·0
Magnesium ...	Mg	24·32	Zinc	Zn	65·37
Manganese ...	Mn	54·93	Zirconium ...	Zr	90·6
Mercury ...	Hg	200·6			
Molybdenum ...	Mo	96·0			

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						4	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569						4	8	12	15	19	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969					3	7	11	14	18	21	25	28	32
							1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553							3	6	9	12	15	18	21	24	28
					1584	1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903					3	6	9	11	14	17	20	23	26
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16	2041	2068	2095	2122	2148						3	5	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430					3	5	8	10	13	15	18	20	23
							2455	2480	2504	2529	2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	16	19	21
						2672	2695	2718	2742	2765	2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
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29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
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41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
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46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

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52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
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61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
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64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
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77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

INDEX

THE END.